

METALS

is to these that this book is addressed in the first instance, but it is also hoped that it will provide those professionally interested in specific aspects of metallurgy with an opportunity of increasing their knowledge of the subject as a whole, and those who read widely with a systematic account of the subject into which they may fit the knowledge acquired in the course of general reading.

It may be said, therefore, that this book deals with the industrially useful metals and alloys from the point of view of the relations between treatment, characteristics, and properties. It deals fully with the subjects considered and is arranged so as to present a logical and systematic account that may be read from beginning to end. It has been prepared with the primary object of enabling students to acquire an ordered understanding and a comprehensive knowledge of the subject. We have endeavoured as far as possible to make the book up to date and accurate in its details, but those who are acquainted with metallurgical research and development at the present time will realize that perfection in this respect is impossible to achieve.

The body of knowledge about metals that exists at the present time has been built up slowly and by the labour of many. In the course of this book, over six hundred publications are referred to, but if an effort had been made to trace the development of modern ideas and to describe the different opinions that now prevail, this number would have been increased tenfold, and the attempt to present a systematic and coherent account of the subject would have been impossible. The views presented in this book are those of the authors, but they have been reached after considering the experiments and views of others, and it is realized that in many instances due credit has not been given them. Consideration of the alternative in the light of existing metallurgical literature will show, however, that no other course could have been adopted in a book designed to cover a wide field and to present a connected account of the subject-matter. Consequently, the opportunity of dealing adequately with the contributions of those who have built up the subject has been sacrificed, and in recognition of their work this book has been dedicated to them.

LONDON, 1939.

H. C. H. C.
J. M. R.

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CHAPTER I

INTRODUCTION

The Importance of Metals.

METALS are not necessary for the maintenance of human life and for a very prolonged period primitive man contrived to exist without knowing how to obtain or how to use them. They are essential, however, for the existence of civilization as we know it, and since their use was first discovered about 5,000 years ago, their influence has been so dominating that it is customary to measure man's progress in terms of the metals he has used.

To begin with, metals were used for ornaments, and later on for implements, tools, and weapons. As civilization advanced more uses were found for them and their production increased, but it was not until the industrial revolution that they began to assume the importance they now possess. Between 1760 and 1860 they were used much more extensively than in previous times, but the amount that found application in that period was only a fraction of what has since been put to use. The present era, which is distinguished by the utilization of metals in enormous quantities, may be said to have begun in 1860. Since then their use has extended at an unprecedented rate concurrently with railway expansion, the use of steel in shipbuilding, the replacement of sailing vessels by steamships, and the development of the electrical, chemical, motor, and aeroplane industries. So rapid has this expansion been that more metal has been produced in the present century than in all previous time.

The most striking achievements of modern civilization depend either wholly or to a large extent on the use of metals. Ships, bridges, railways, locomotives, automobiles, cables, power stations, aeroplanes, electrical distributing systems, telephone and telegraph systems, &c., are some of the most conspicuous products of the combined efforts of metallurgists and engineers. Enumeration of such obvious uses, however, gives only a very inadequate picture of their contribution to modern life, and even when mention has been made of personal, domestic, and artistic uses, the most important applications of metals have still to be stated, for the principal service which they render is in the construction of the plant and machinery used in other industries. In the mining of coal and metals, in agriculture, in the oil, electrical, chemical, food, and textile industries, plant and machines constructed of metal are essential, and the same applies to the manufacture of the hand and machine tools used in building this plant and machinery. In general, although only a portion of the final products that constitute the material world to-day are actually constructed of metals, the manufacture of everything depends to some extent on their use.

The Elementary Metals.

All matter is composed of atoms. There are 92 different kinds of these, and their various combinations make up the innumerable gaseous, liquid, and solid substances which constitute the universe. Any substance that is composed entirely of atoms of one kind is an elementary substance, and therefore there are 92 elementary substances or elements. Each of these elements has certain attributes or properties that distinguish it from the others, and among the most important are those that determine its relations to other elements in the formation of compounds. There are 6 elements that do not form compounds, viz. helium, neon, argon, krypton, xenon, and niton. These constitute the group of inert gases. Of the other 86 elements 2 have not been isolated and the remainder are classified as metals and non metals according to their behaviour relative to each other in the formation of compounds. The non-metallic elements are hydrogen, boron, carbon, nitrogen, oxygen, fluorine, silicon, phosphorus, sulphur, chlorine, bromine, and iodine. The remaining 72 elements are metals. Of the 90 elements that have been discovered three have been detected only in the spectra of stars. The 87 that have been found on the earth occur in greatly varying proportions. Oxygen, nitrogen, hydrogen, silicon, aluminium, iron, magnesium, calcium, sodium, potassium, and carbon are abundant, and their various compounds account for all but a small fraction of the accessible crust of the earth, the sea, and the atmosphere. All the remaining elements constitute only a small portion of our material environment and some of them are extremely rare.

The Useful Metals.

In so far as chemistry is concerned with metals it deals mainly with metallic elements as constituents of compounds. Metallurgy is concerned with the decomposition of compounds in order to obtain the metals, and with the properties and uses of the metals thus obtained. To engineers and other users metals are solid substances having properties of a certain kind as exemplified by steel, brass, copper, aluminium, lead, silver, gold, &c. These metallic substances in everyday use are related to the elementary metals in that they consist of them, but in most of the metal used in the metallic state (i.e. not in compounds) only a small number of the elementary metals are involved. A large number of metallic elements have some useful application either in the pure state or as an alloy. In some cases a more extended use is prevented by the scarcity of the metal. The metals that are now available in comparatively large quantities and for which a wide variety of uses have been found are iron, copper, lead, zinc, aluminium, tin, nickel, and magnesium. These and their alloys are the industrially important metals.

Metals and Alloys.

Scientifically defined a pure metal is a metallic element with a purity of 100 per cent. This degree of purity has been closely approached in the preparation of many metals, but it has never been attained. Thus an absolutely pure metal is an abstraction. Scientifically defined an alloy is any metallic substance other than a pure elementary metal, and in this sense all metals in use to-day are alloys. Popularly, however, the term alloy is used in rather a different sense to denote intentional mixtures of metals made in order to secure certain desirable properties. This use of the term has arisen because in recent years great improvements in properties, and a great increase in the variety of alloys, have been obtained by mixing metals in suitable proportions.

At the present time there is some confusion attached to the use of the terms metal, alloy, and impurity. It is therefore worth while to consider how they may be used most satisfactorily. In the first place it may be stated that metal in its general sense means all metallic substances. These generally consist predominantly of one metallic element, the basis metal, plus a certain number of secondary constituents which may either be metals or non-metals. Some of these secondary constituents are classed as impurities and others as additions, and metallic substances are generally classified as pure metals, impure metals, and alloys. Difficulties in the use of these terms arise because the word alloy may cover pure metals as at present available, impure metals, and intentionally prepared alloys, while impurities may mean intentional additions as well as undesirable constituents. It is difficult to avoid this confusion, but important to explain the relations between the terms and the actual composition of metallic substances.

The secondary constituents in metallic substances may be classified as follows according to their origin:

1. (a) Those associated with the basis metal in the ore and not eliminated in the course of manufacture, or (b) picked up during the manufacturing operations.
2. Those intentionally added to eliminate or counteract the effect of some other constituent.
3. Those intentionally added to obtain certain desirable properties.

The constituents that derive from the ore or are absorbed during manufacture may be called impurities, but they are not always undesirable, and must therefore be divided into two groups. In some cases a certain impurity is always undesirable, e.g. sulphur in nickel. Sometimes, however, its effect depends on the use for which the metal is intended. It is, e.g., extremely difficult to produce iron free from carbon, and when pure iron is required for magnetic purposes the carbon is an undesirable impurity. In the iron alloys, steel and cast iron, however, it is an essential constituent. It will be evident from (2) above that although the quality of metals cannot be controlled to such an extent

as to permit their preparation in a condition of absolute purity there is frequently some choice with regard to what elements will finally remain. Oxygen, e.g. can usually be eliminated by the addition of substances known as deoxidizers and certain amounts of these remain in the metal. But it is not always desirable to eliminate oxygen by this means, for the added element may have a more deleterious effect on certain properties than the oxygen. In making high conductivity copper deoxidizers are not used because they increase the electrical resistance to a greater extent than does the oxygen. When deoxidizers or other substances are added to eliminate an impurity or counteract its effects they have a beneficial effect and may therefore be classed as additions. Elements added to obtain desirable properties are also additions.

When dealing with metals from a particular point of view it is usually convenient to adopt either the scientific or the popular use of the term alloy. Owing to the scope of this book, however, both uses will have to be adopted. Thus, in describing the theory of alloys, everything that is not a pure metal will be regarded as an alloy, but in dealing with industrial metals the word alloy will be applied only to basis metals to which other elements have been added to secure certain desirable properties. In general, only two types of metallic substances will be distinguished, viz. pure metals and alloys, but in considering these substances from an industrial point of view the following types will be taken into account:

1. Pure Metals. Metallic elements of a purity approaching 100 per cent.
2. Impure Metals. Metallic elements containing (a) undesirable impurities that it is technically or economically impossible to eliminate, (b) additions made to eliminate or counteract the effect of undesirable impurities, or (c) impurities not necessarily undesirable.
3. Alloys. Metallic substances consisting of an intentional:

Classification of Metallic Elements.

The metallic elements usually classed as industrially important are iron, copper, lead, zinc, aluminium, tin, nickel, and magnesium. All these metals are used in the pure or commercially pure condition for certain purposes and they are the basis of many alloys. Furthermore, the secondary constituents of many of the most important industrial alloys are included in this group. Thus brass is an alloy of copper and zinc, bronze an alloy of copper and tin, and aluminium bronze an alloy of copper and aluminium. Copper is one of the most important secondary constituents of light aluminium alloys. Copper and nickel, and nickel, and zinc form important alloys, while lead and tin are in most white bearing metals, type metals, solders, &c. Zinc, aluminium, tin, and nickel are used extensively as coatings on other metals.

None of the other metallic elements are used in so many ways as those mentioned above. Some of them, e.g. tungsten and molybdenum are used for certain special purposes, while others are employed for plating, as secondary constituents in alloys or as deoxidizers. These include chromium, cobalt, cadmium, manganese, titanium, vanadium,

TABLE I

<i>Metal</i>	<i>Symbol</i>	<i>Atomic number</i>	<i>Specific gravity</i>	<i>Elec. cond. silver at 0° C. = 100</i>	<i>Melting-point ° C.</i>
Aluminium	Al	13	2.7	57	660
Antimony	Sb	51	6.62	4	630
Arsenic	As	33	5.73	5	850
Beryllium	Be	4	1.8	..	1,285
Bismuth	Bi	83	9.82	1.3	268
Cadmium	Cd	48	8.64	20	321
Calcium	Ca	20	1.55	18	851
Chromium	Cr	24	7.14	..	1,800
Cobalt	Co	27	8.79	15	1,467
(Columbium) (Niobium)	Cb	41	12.75	..	1,950
Copper	Cu	29	8.93	94	1,083
Gold	Au	79	19.32	67	1,063
Iron	Fe	26	7.86	17	1,537
Lead	Pb	82	11.37	7.2	327
Lithium	Li	3	0.534	16	186
Magnesium	Mg	12	1.74	34	649
Manganese	Mn	25	7.39	..	1,240
Mercury	Hg	80	13.56	1.5	—38.5
Molybdenum	Mo	42	10.0	..	2,450
Nickel	Ni	28	8.9	20.5	1,455
Osmium	Os	76	21.6	..	2,500
Palladium	Pd	46	11.4	..	1,555
Platinum	Pt	78	21.5	13.5	1,773.5
Rhodium	Rh	45	12.44	..	1,966
Silver	Ag	47	10.5	100	960
Sodium	Na	11	0.971	28	97.5
Tantalum	Ta	73	16.6	..	2,910
Tellurium	Te	52	6.25	0.077	450
Tin	Sn	50	7.29	11.3	232
Titanium	Ti	22	4.8	..	2,000
Tungsten	W	74	18.8	..	3,400
Vanadium	V	23	5.5	..	1,720
Zinc	Zn	30	7.1	25.5	419.4
Zirconium	Zr	40	6.53	..	1,927

bismuth, antimony, beryllium, tantalum, niobium, arsenic, calcium, tellurium, sodium, lithium, mercury, and zirconium. Of non-metals present in industrial metals, carbon, silicon, and phosphorus constitute important additions, nitrogen is used in producing a hard coating on steel, silicon and phosphorus are employed as deoxidizers, and oxygen and sulphur are common impurities.

When account is taken (1) of the metals used in the pure state, as the basis of alloys and for coating other metals, (2) of the metals and

non-metals used as secondary constituents in alloys and as deoxidizers, and (3) of the metals and non-metals which occur as impurities, a list of thirty-four elements results. It is with these elements that this book is mainly concerned, but in illustrating general questions references will sometimes be made to the precious metals, gold, silver, platinum, palladium, iridium, rhodium, and osmium. A list of the metallic elements mentioned above together with some particulars relating to them is given in Table I based on data given in the *Metal Industries Handbook* (1). A full list of the chemical symbols and atomic numbers of the elements is given in Table II.

TABLE 2
Industrial Alloys

<i>Name</i>	<i>Basis metal</i>	<i>Essential additions</i>	<i>Other constituents</i>
Steel	Iron	C	Mn, Si, S, P
Alloy Steel	Iron	C, Ni, Cr, Mo, V, Mn, Si, Cu	Ti, Al
Stainless Steel	Iron	Cr	C, Ni, Si, Al, W, Ti, Mo
High Speed Steel	Iron	C, W, Cr, V	Mo, Co
Cast Iron	Iron	C, Si	P, Mn, S
Alloy Cast Iron	Iron	C, Si, Ni, Cr, Mo, Mn, Cu	P, S
Brass	Copper	Zn	
Special Brass	Copper	Zn	Al, Sn, Si, Pb, Mn, Fe, Ni
Tin Bronze	Copper	Sn	Zn, P, Pb
Aluminium Bronze	Copper	Al	Mn, Fe, Ni, Si, Sn, Zn
Aluminium Alloys	Aluminium	Cu, Si, Mg	Mn, Fe, Zn, Ni
Nickel-Copper	Nickel-Copper		Al, Si
Nickel-Silver	Copper	Ni, Zn	
Nickel-Chromium	Nickel	Cr	Fe, Al, Si, W, Mo, Mn
Cable Sheath Alloys	Lead	Cd, Sn, Sb	Cu, Te
Type Metals	Lead	Sb, Sn	
Solders	Lead	Sn	Cd, Bi
Fusible Alloys	Bismuth	Pb, Sn	Cd, Hg
Bearing Metals	Lead	Sb, Sn, Bi	
	Tin	Pb, Cu, Sb	
Zinc Alloys	Zinc	Cu, Al, Sn	
Magnesium Alloys	Magnesium	Al, Zn, Mn, Si	Cd, Ca, Ce, Ag, Co

Industrial Alloys.

To indicate how the important industrial alloys are built up from the elements shown in Table I, a list of these is given in Table 2. Where several constituents are mentioned under essential additions or other constituents it does not mean that all these elements are present in any particular alloy, but that all of them are used in varying amounts and combinations in making alloys of this type.

The Occurrence of Metals.

The earth as a whole consists mainly of metal, but most of it is situated in the interior and is therefore inaccessible. Calculation of the density of the earth together with the evidence obtained from meteorites, which are portions of disintegrated planets, indicates that its core consists mainly of an alloy of iron and nickel. The crust, however, is of an entirely different composition. At one stage of its history the earth consisted of a molten ball in which all the elements were intimately mixed, but as it cooled the constituents gradually sorted themselves out into a layer of silicates and sulphides on the surface and a core of metal in the centre. Such a differentiation is an important feature of metallurgical smelting operations. The crust of silicates contained very little metal, but as it cooled a further differentiation of its constituents took place. This led to the separation of silicates and sulphides and most of the metal segregated with the sulphide. Thus some concentration of the metals occurred. Later such geological processes as intrusion, magmatic differentiation, the movement of hot solutions coming from magma, weathering, and the downward movement of surface water, resulted in further concentration of the metals in the accessible crust and the workable metalliferous deposits known as ores were produced.

TABLE 3
Composition of the Earth's Crust

Silica. SiO_2	59.77
Alumina. Al_2O_3	14.89
Iron Oxide. Fe_2O_3 and FeO	6.08
Magnesia. MgO	3.74
Lime. CaO	4.85
Soda. Na_2O	3.25
Potash. K_2O	2.98
Water. H_2O	2.02
Titanium dioxide. TiO_2	0.77
Carbon dioxide. CO_2	0.7
Phosphorus Pentoxide. P_2O_5	0.28
Sulphur. S	0.10
	99.43

The calculated composition of the accessible crust is shown in Table 3. Only three of the metals of technical importance at present, viz. aluminium, iron, and magnesium, occur in large proportions. All the other valuable and useful metals constitute part of the 0.57 per cent. not taken into account in the Table. If these metals were uniformly distributed, metallurgy as we know it would not exist. It would be going too far to say that under such conditions metals would not be used by man, but their economic position would be entirely different. Even with the most modern methods of ore concentration the metals that are now common would be rare, while those that are now rare would be practically unknown. It is probable that in the first formed

rock crust the metals were more or less uniformly distributed, but there is no evidence that any part of this is still accessible. Its outer layers have been worked over and over again by processes of geological distribution and reconstruction and, as a result, metals have been concentrated here and there in considerable quantities. It is these concentrations that have been exploited by man to a constantly increasing extent during the last 5,000 years.

A workable ore deposit is a portion of the accessible crust in which some metal (or metals) is (or are) present in such quantity and in such a state of combination that it is capable of profitable extraction with the methods available. The development of more efficient methods of extraction makes it possible to exploit poorer deposits. A rise in the market value of a given metal has a similar effect, while a fall renders it impossible to extract it profitably from the poorer deposits that were worked before the price fell. Table 4 shows the extent to which the metals are concentrated in average workable deposits in relation to their concentration in the earth's crust as a whole.

TABLE 4

Concentration of Metals in Workable Deposits in Relation to their Concentration in the Accessible Crust of the Earth

<i>Metal</i>		
Aluminium	4	5 to
Iron	5	10
	50	
pp	100	700
Vanadium		
	250	800
Gold	2,500	7,50
Silver		15,00

A metalliferous ore as obtained from a mine consists of two intimately mixed portions (1) the mineral matter which may be metal or a compound containing metal, (2) the gangue which is extraneous matter mixed with the mineral but containing no metal. Most of the deposits from which metals are obtained contain them in the form of a compound such as oxide, sulphide, sulphate, silicate, or carbonate. The gangue consists mainly of silicates. Certain metals occur, however, in the native state, i.e. not in a compound. Gold and platinum are generally found in this form because they do not readily combine with other substances. Copper and silver occur native in several localities as a consequence of certain geological conditions, while iron-nickel meteorites are scattered here and there on the earth's surface.

Concentration, Extraction, Refining.

Numerous operations are involved in obtaining metals from their ores. There is a particular sequence of operations pertaining to each

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metal, and in many cases there are several different sequences of operations designed to deal with different compounds of the metal or with ores containing it in association with different combinations of other metals. Generally, however, the first operations are designed to separate as much of the gangue as possible from the mineral matter. These are known as concentrating processes. Following this, other operations are performed to decompose the compound, separate the rest of the gangue, and obtain the metal in a relatively impure condition. This is known as extraction. Finally various operations are performed to purify the metal. This is refining.

Ore concentration, extraction, and refining do not come within the scope of this book, but it is necessary to explain that the processes involved in obtaining metals are such that they can be produced in varying conditions of purity according to the degree of trouble taken in refining them. For some purposes metal of high purity is required and can be sold at a price that will pay for the most careful and elaborate refining. For others, metal of lower purity will serve, and as it does not require so much refining it is sold at a lower price. In the manufacture of the non-ferrous metals, e.g. copper, aluminium, lead, zinc, nickel, and tin, the object of the various processes is to produce each of these metals in the condition of purity required. Alloys are made by mixing them and adding such other elements as are necessary. In the manufacture of the ferrous metals, however, the product of the extraction is cast iron, and although it is usually remelted before being cast into the shape required, it can be used just as it comes from the blast-furnace in which the iron ore is smelted. Thus the impure iron resulting from the extraction operation is an important industrial alloy. The purification of this cast iron leads to the production of another important industrial alloy, steel. Pure iron is produced by further purification. Thus in ferrous metallurgy the important alloys are to some extent intermediate products in the manufacture of the pure metal, and intentional alloying by the addition of other elements is not carried out except in the manufacture of the special types of cast iron and steel known as alloy cast iron and alloy steel.

The Properties of Metals.

Thirty-four metals are shown in Table 1. From these a very large number of alloys may be made, and *Engineering Alloys* (2) contains a list of some 8,200. Each metal and alloy has certain properties, e.g. density, melting-point, boiling-point, specific heat, latent heat of fusion, linear coefficient of expansion, electrical conductivity, thermal conductivity, magnetic susceptibility, strength, hardness, &c. A vast amount of work has been carried out in determining these, but some of the available data are inaccurate, and much more remains to be done. In considering the individual metals and alloys their specific properties will be dealt with, but in the meantime attention may be

On those general groups of properties that affect the preparation of metals for use and their behaviour in service.

Most metals are molten at the end of the manufacturing operations, and alloys are made by mixing metals in the molten condition. Thus a metal or alloy may be said to be made when a melt of the requisite composition has been prepared. The molten metal is then poured into a mould and allowed to solidify. The properties that affect the performance of this operation are its casting properties. The metal may be cast in the shape in which it will be used and go into service without any further treatment except machining of the whole or part of its surface. Alternatively, it may be cast in a simple shape and subsequently brought to its final shape by mechanical pressure applied to the metal while hot or at atmospheric temperature. The properties that control its response to these operations are its working properties.

The shaping of metals depends on their casting, hot working, cold-working, and machining properties. In producing metal structures, welding, soldering, and brazing properties come into play. All these are related to the treatment of metals, and the operations performed during treatment influence properties as well as shape. properties are involved in the use of metals. Tungsten is used of its high melting-point, whereas fusible alloys of bismuth, lead, and tin are used because of their low melting points. Certain alloys of nickel are used because they neither contract nor expand over a certain of temperature. Aluminium and magnesium find application to a siderable extent because of their low specific gravity, whereas lead is sometimes used because of its high specific gravity. In general, however, the use of metals is controlled by six groups of properties, which come into the categories mechanical, chemical, thermal, electrical, magnetic, and antifrictional. The mechanical properties are those that determine response to applied force, the chemical those that determine resistance to the environments to which metal is exposed, the thermal include heat conductivity and coefficient of expansion, the electrical and magnetic control the use of metals in electrical engineering, while the antifrictional determine the use of metal bearings. In all these of metals at least one and usually several of these groups of is important. Sometimes specific gravity and decorative value have also to be considered, and price is always an important matter.

The Treatment of Metals.

The art of metallurgy embraces the extraction and refining of metals, the manufacture of alloys, and the treatment of these in preparation for use. The ultimate object is to produce metals capable of useful application. If the behaviour of a metal in service depended only on its composition, all that would remain to be done after a melt of the required composition had been prepared, would be to bring the metal to the required shape by casting, working, and machining. Behaviour in ser-

vice depends, however, on the way in which the casting and working operations are carried out for these have a pronounced effect on its useful properties. It also depends on certain operations that have nothing to do with shaping. These include thermal treatment which consists of operations designed to influence the properties of the solid metal by controlled heating and cooling. Thus the treatment of metals consists in general of casting, working, and thermal treatment, but several other operations which are sometimes performed, e.g. joining by welding, soldering, and brazing, surface treatments, and machining are also important.

The Nature of Metals.

When a metal specimen is suitably prepared and examined under the microscope it is seen to be an aggregate of grains. These are the crystals of the metal. In a specimen of pure metal all the crystals are similar in that they consist of the same kind of atoms packed together in the same way. The atoms, of course, cannot be seen even under the most powerful microscope, but their arrangement in the crystal can be ascertained by means of X-rays. In some alloys all the crystals are similar and each contains atoms of all the elements in the alloy. In other alloys two or more different kinds of crystals may be present. Sometimes these are each composed of atoms of one of the elements present, but usually, each kind of crystal contains two or more different kinds of atoms in certain proportions.

In a particular specimen of a pure metal the crystals do not vary much in size and shape. But in different specimens of the same metal the size and shape of the crystals vary according to the treatment they have received. In alloys that consist of crystals of one kind the same conditions prevail, while in those that consist of several kinds of crystals the arrangement of these with respect to each other has to be taken into account in addition to the shape and size of the crystals of each kind. This arrangement is also affected by treatment. The kind of crystals present in a given specimen of a particular alloy and the relative proportions of each are its constitution. The arrangement of the atoms within these crystals constitute its crystal structure, while the size, shape, and arrangement of the crystals constitute its microstructure. All these are affected by the conditions set up during casting, the extent to which the metal has been worked, the temperature at which it was worked, and the thermal treatment to which it has been subjected.

Metals have a number of other characteristics. They nearly always contain appreciable quantities of non-metallic materials known as inclusions, and they may also contain cracks and cavities formed during casting, working, or thermal treatment. These determine their condition. A metal that is relatively free from inclusions, cavities, and cracks is said to be clean and sound, whereas one that contains many of them is said to be dirty and unsound. In order that a specimen of

metal may be described accurately its composition, constitution, crystal structure, microstructure, and condition must be known, and these five characteristics determine its nature.

Properties, Nature, and Treatment.

Knowledge about any given metal or alloy centres round the nature of each individual sample in the condition in which it will be used. This is related on the one hand to its treatment and on the other to the properties that determine its behaviour in use. These relations are illustrated in the following table:

Properties	Mechanical		
	Chemical	Composition	
	Electrical	Condition	Composition
	Magnetic	Constitution	Casting
		Microstructure	Hot working
	Antifrictional	Crystal structure	Cold working
			Heat treatment

The useful properties are directly related to the composition, and to the condition, constitution, microstructure, and crystal structure. These are in turn related to the composition and treatment. It is with the subjects shown in the above table and the relations between them that this book is concerned. The general consideration of metals and alloys would be greatly simplified if it were possible to consider separately each of the factors that constitute the nature of a sample in relation to each stage in its treatment and each of its properties. Actually, however, nature, treatment, and properties are so intimately connected that all of them must be taken into account at the same time. When composition is considered alone without regard to treatment, its importance varies greatly according to the properties that are taken into account. When electrical conductivity is concerned, composition is all important. Magnetic properties and chemical properties are also determined to a large extent by composition, but condition, constitution, microstructure, and crystal structure are also important. Mechanical properties, however, are influenced to a great extent by those other factors, which in this connexion are at least as important as composition. Thus, whereas the nature of the electrical, magnetic, or chemical properties required practically determines the composition of the alloy to be used, when mechanical properties only have to be considered there is a choice of several alloys which will give the required results.

Factors affecting the Selection of Metals.

The use of metals is affected by the available ore resources, the cost of extraction and refining, and the ways in which they can be employed to practical advantage. However plentiful the ores may be, the extraction of a metal will not be profitable unless it is sufficiently suitable for some purpose to be sold at a price that will pay for extraction. However useful it may be, it cannot be employed to advantage unless it can be obtained in adequate quantities and at a price commensurate with its utility. In short the relations between the extraction and application of metals are controlled by the ordinary economic laws of supply and demand. The more extensive application of a metal may be prevented by (1) the scarcity of the available ores, e.g. radium, (2) the high price maintained, e.g. nickel, (3) the absence of suitable methods of extraction, e.g. beryllium, or (4) the restricted demand arising from the lack of useful applications, e.g. many of the rarer metals. All these factors are, however, closely related, for there is nothing to stimulate the study of new uses of a metal that is known to be rare, and while the demand remains small, the price will remain high because large and efficient plants will not be established and improved methods of extraction will not be sought.

The industrially important metals are used in many ways, either in the commercially pure condition, as the basis metals of alloys, as secondary constituents in alloys, or as coatings on other metals. In comparison with the amount of iron used as the basis metal in cast iron and steel, that used in the pure condition or in other alloys is insignificant. Copper on the other hand is mainly used in a highly purified condition, about 80 per cent. of the total production being thus employed. Lead is also mainly used in a comparatively pure state or with the addition of small amounts of alloying elements, while the chief uses of zinc are as a protective coating on steel and as the second constituent in brass. Aluminium is chiefly used as the basis of light alloys, tin as a coating on steel or a constituent of solder and bearing metals, while the principal use of nickel is as an addition to steel. Other uses are, copper as the basis metal in brass and bronze, lead in the manufacture of white and red lead, zinc in the form of zinc sheet, and nickel in alloys with copper, chromium, or iron, and as a protective coating on steel.

There are great fluctuations from year to year in the amounts of metal produced, and curves showing production over a long period have many maxima and minima. When the best line is drawn through the points, however, a continuous and rapid increase in production is seen to be taking place. Fig. 1 illustrates the general trend of the production of pig iron and steel between 1800 and 1929. Fig. 2 shows the same thing for the non-ferrous metals. Two graphs are necessary because the production of iron and steel is on a so much larger scale than that of the other metals. Table 5 gives the figures for the production of the

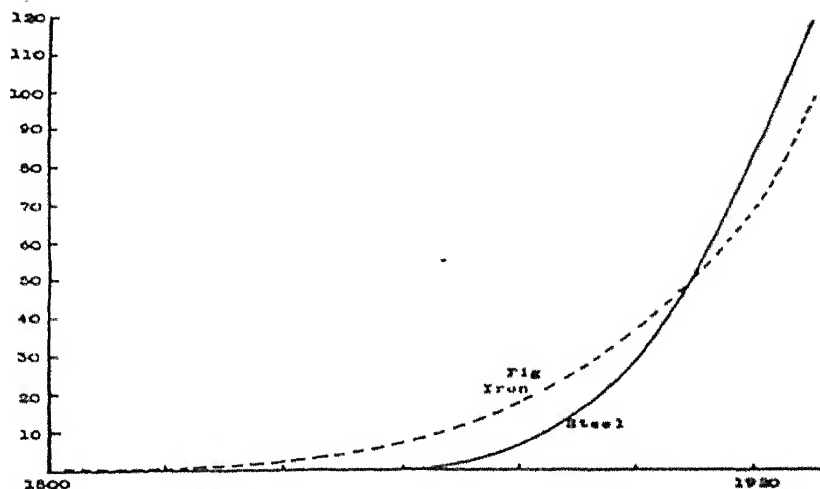


FIG. 1. ney of iron and
1800-1929. of tons. (British Sci Guild.)

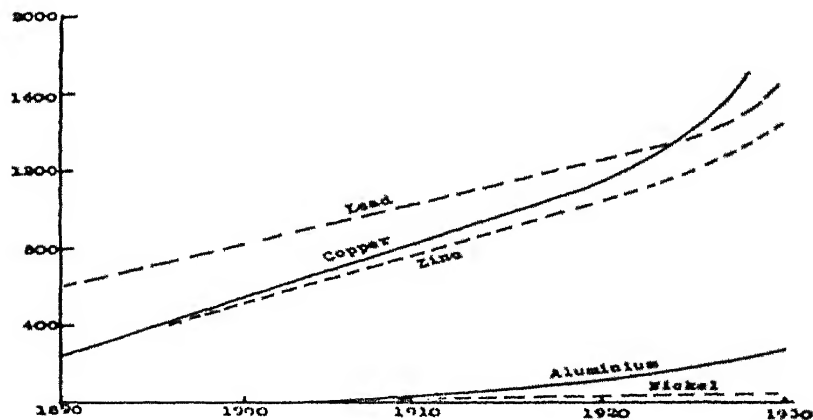


FIG. 2. World's production of some non-ferrous metals in
thousands of tons. (British Science Guild.)

industrial metals in 1929, 1934, and 1935. In 1929 production reached a record figure; in the following years it declined rapidly but began to rise again in 1934 and 1935.

TABLE 5

World's Production of Industrially Important Metals

(in thousands of tons)

	1929	1934	1935
Steel . .	118,312	80,797	97,887
Pig-Iron . .	95,900	64,240	72,111
Lead . .	1,753	1,351	1,420
Copper . .	1,921	1,258	1,454
Zinc . .	1,470	1,183	1,349
Aluminium .	270	172	257
Tin . .	190	116	146
Nickel . .	63	73	79

PART I

MICROSTRUCTURE, CRYSTAL STRUCTURE, DEFORMATION AND FRACTURE OF METALS

CHAPTER II

THE MICROSTRUCTURE AND CRYSTAL STRUCTURE OF PURE METALS

THE purpose of the three chapters of which Part I consists is to describe the characteristics of solid pure metals and to explain how they behave when subjected to the action of mechanical forces under different conditions of time and temperature. It is explained in the first place that when a specimen of pure metal is suitably prepared and examined under the microscope it is seen to consist of an assemblage of crystals the size and shape of which constitute its microstructure. As the characteristic of a crystal is that the atoms of which it is composed are arranged in a regular way, the arrangement of the atoms in metal crystals is then described and some of the principal features of the crystal structure are considered. Having shown that solid metals are aggregates of crystals, and having explained what these crystals are, attention is then given to the conditions that prevail at the surface of contact between adjacent crystals, i.e., the crystal boundaries. This completes the general description of the nature of solid pure metals. Up to this point crystals are regarded as being built up of atoms arranged in a regular pattern, but in order to give a more precise account of crystal structure it is necessary to consider how the atoms are linked or bound together in the crystals. Some account of this is therefore given and the difference between metallic and non-metallic crystals explained. Chapter II is then concluded with a description of the characteristics of metal surfaces. In Chapter III the behaviour of metals when subjected to the action of mechanical forces is discussed and the effect of time and temperature on this behaviour is dealt with in Chapter IV.

Methods of Study.

In the study of solid metals numerous methods are employed. Some of them are used to investigate the changes that occur during solidification and subsequent cooling to atmospheric temperature, others to examine the metals as they exist at atmospheric temperature. Of the methods used for the latter purpose the most direct information is obtained by chemical analyses, X-ray analyses, and microscopic examination. The complete chemical analysis of a particular sample gives

the proportions in which the various elements are present. Thus it reveals the relative proportions of copper and zinc in a sample of brass and those of iron, carbon, manganese, silicon, phosphorus, and sulphur in a sample of steel. The results of chemical analyses are expressed in percentages by weight, but they can be converted to atomic percentage, i.e. the number of atoms of each element per 100 atoms of the sample, by taking account of the atomic weights. X-ray analyses show how these atoms are arranged in the crystals of the metal, i.e. the crystal structure, while microscopic examination shows how the crystals are arranged in the sample, i.e. the microstructure.

These three methods of study are supplemented by a number of others which give less direct information about composition and structure but more information about properties. Among them may be mentioned measurements of magnetic and electrical properties, mechanical tests, and determinations of specific volume. When such methods are used some property is studied and information about the metal concerned is obtained by inference based on some previously established relationship between that property, and structure, constitution, or condition.

The study of the behaviour of metals during solidification and subsequent cooling provides knowledge about the changes that occur in the metal while these are taking place. Frequently, however, it also furnishes information about the nature of the metal at atmospheric temperature. In these studies the change of some property with temperature is determined and information about the nature of the metal obtained by inference. Almost any property may be studied in this way, but in general, changes with temperature are investigated by thermal, electrical, magnetic, or volume measurements.

The Microstructure of Pure Metals.

Before the microstructure of a metal can be studied its surface must be prepared in a suitable form, and the methods used for this purpose will be described presently. Meanwhile, it must suffice to say that this preparation involves three operations, namely, grinding, polishing, and etching. When a suitably prepared specimen of pure iron is examined under the microscope, the structure shown in Fig. 3 is observed. The surface is seen to be divided up into a number of small areas separated

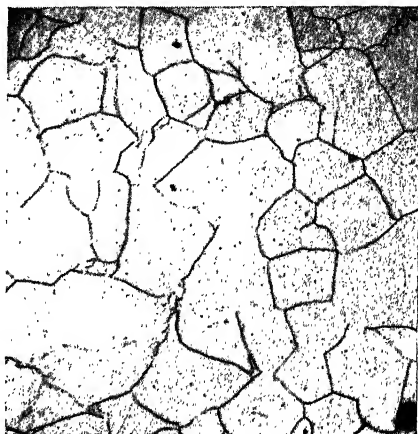


FIG. 3. Microstructure of pure iron.
× 100.

from each other by dark lines. Each of these areas is a section through one of the polyhedral grains or crystals of which the metal is composed. The dark lines are shadows caused by differences in level between the crystals, which are due to the fact that the various crystals are dissolved at different rates by the etching reagent.

By using a different method of etching a structure may be produced in which the individual crystals are distinguished from each other by a difference in colour. The kind of structure then obtained is shown in Fig. 4 and the cause of this difference in colour is explained on p. 47.



FIG. 4. Microstructure of pure copper. $\times 100$.

This figure is a micrograph of pure copper, but a similar structure could also be produced in pure iron, and the structures shown in the two figures may be regarded as representative of pure metals in such a condition that no evidence of mechanical deformation is

THE CRYSTAL STRUCTURE OF PURE METALS

Before proceeding further it is necessary to consider the meaning of crystal structure in order to explain what is meant by a crystal and to show how the various crystals in a pure metal are distinguished from each other. The crystalline state is to a large extent synonymous with the solid state. Under certain conditions crystals may exist in liquids, and a few solids exhibit little evidence of crystallinity, but in general solids are crystalline and liquids are not. The criterion of the crystalline state is the arrangement of the atoms in a regular pattern in space, and in most of the metals this is of a comparatively simple nature. The existence of a regular arrangement of atoms in many solids was inferred long ago from the study of the faces of crystals, cleavage, optical properties, &c., but the exact arrangement of the atoms in a given solid could not be determined until the science of X-ray crystal analyses.

developed. The credit for the original experiment which demonstrated that X-rays were diffracted by crystals is due to M. Laue, but the initiation and early development of the science were mainly accomplished by Sir William Bragg and his son, Professor W. L. Bragg. Laue's experiment was performed in 1912, and by 1915 the Braggs had worked out the basic method of crystal analysis by means of X-rays. Since then the subject has been studied by numerous investigators, new methods of carrying out the analyses have been devised, the experimental technique and the interpretation of results have been perfected, and the examination of the crystal structure of a large number of substances including many metals and alloys has been carried out.

The methods employed in X-ray crystal analysis are described in a number of books among which may be mentioned, *The Crystalline State*, vol. i, by W. L. Bragg (3); *Study of Crystal Structure and its Applications*, by W. P. Davey (4); and *Applied X-rays*, by G. L. Clark (5). In this book attention will be confined to a consideration of the results obtained.

Simple Arrangements of Atoms in Metal Crystals.

In most of the elementary metals and the alloys based on them the atoms are arranged in a very simple pattern which may be imitated by packing spheres. Actually atoms are not minute compact spheres, and at a later stage it will be necessary to consider what they really are. For the time being, and from the point of view of their packing in metal crystals they may, however, be regarded as spheres.

Fig. 5 shows one way in which atoms are packed in metal crystals. The full circles represent one layer of atoms placed in parallel rows while the broken ones represent a second layer placed on top of the first in such a way that the centres of the atoms in the second layer are vertically above the points of intersection of diagonals joining the centres of atoms in the first layer. Thus the centre of the atom *E* is vertically above the point of intersection of the lines *AB* and *CD*. The third layer is placed vertically above the first, the fourth vertically above the second and so on; in this way a structure that consists of a repetition of the two layers shown is built up. This is how the atoms are arranged in crystals of iron, chromium, tungsten, molybdenum, and a number of other metals.

Owing to the way in which Fig. 5 is drawn there are more circles in the first than in the second layer, but as the packing in the second layer is the same as in the first there are the same number of atoms in each layer of an actual crystal. In order to give an idea of the dimensions of the pattern shown in Fig. 5 it may be said that in pure iron at atmospheric temperature the distance represented by *AC* is 2.86 Ångström units (1 Ångström unit = 10^{-8} cm. or one ten-millionth of a millimetre). Thus a row of iron atoms one millimetre in length in the direction *AC* would contain 3,496,500 atoms.

If two series of lines parallel to the top and the side of the respectively are drawn through the centres of the atoms in the first layer (Fig. 5), the plane on which these centres lie is divided up into squares. The centres of the atoms in this layer may therefore be said to be situated at the corners of a set of squares of which $ACBD$ is one. The centres of the atoms in the third, fifth, seventh, and successive layers are also situated at the corners of squares (that are vertically above those representing the disposition of the atoms in the first layer. If now

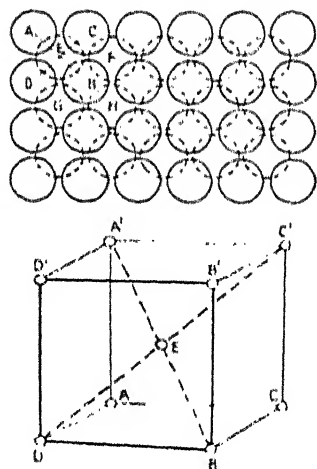


FIG. 5. Packing of atoms in metal crystals. Body-centred cubic arrangement.

a series of vertical lines is drawn through the centres of corresponding atoms in the first, third, fifth, and successive layers, these lines, with those already drawn through the centres in each layer, divide space up into cubes. Each of the cubes thus obtained completely encloses one of the atoms in the second, fourth, sixth and successive layers. Thus the centres of the atoms $ACBD$ are situated at the corners of a square, and the centres of the corresponding atoms $A'B'C'D'$ in the third layer are likewise situated at the corners of a square vertically above $ACBD$. When A is joined to A' , C to C' , B to B' and D to D' a cube is formed as shown in the lower part of Fig. 5 in which the centres of the atoms are represented by circles. The second layer atom E is enclosed within this cube.

A regular pattern of points in space is a space-lattice and the points are known as lattice points. In crystals the atoms in a regular pattern in space and their centres therefore form a lattice. The space-lattice for the particular arrangement of shown in Fig. 5 can be constructed by dividing space into cubes and placing a lattice point in the centre of each cube and at each corner where eight cubes meet. The lower portion of Fig. 5 shows one such cube and the arrangement of atoms in the crystal may be said to consist of a repetition of this cube, which is known as the unit cell of the space-lattice.

In the unit cell shown in Fig. 5 there are eight atoms at the corners and one in the centre of the cell. In a crystal, however, there are an equal number of atoms in the cube-corner and cube-centre positions. This difference between the crystal structure and the unit cell arises from the fact that, while the cube-centre atom E is entirely contained in one unit cell, each corner atom is shared by eight cells, i.e. its centre is located at the point where eight cubes meet. For the purpose of description the first, third, and fifth layer atoms have been selected as the cube-

corner atoms, but the second, fourth, and sixth layer atoms might equally well have been taken as cube-corner atoms, and the first, third, and fifth layer atoms as cube-centre atoms. Had this been done *EFHG* would have formed one side of a cube in which the third layer atom vertically above *B* would be the cube-centre atom.

The arrangement of atoms just described is known as the body-centred cubic arrangement because the unit cell is cubic and contains a lattice point at the centre as well as at the corners. If the second layer and all corresponding layers (fourth, sixth, &c.) are left out of the arrangement there are no cube-centre atoms. The unit cell then consists of a cube with a lattice point at each corner. This is the simple cubic arrangement. It does not occur in metal crystals, but is fairly common in inorganic salts.

In the crystals of a number of metals the atoms are arranged on a body-centred cubic space-lattice, but owing to differences in the size of the atoms the dimensions of the unit cell vary from metal to metal. The length of the side of the unit cell is the lattice constant, and in the body-centred crystals of iron, tungsten, molybdenum, and vanadium it is respectively 2.86, 3.16, 3.14, and 3.04 Ångström units. In the body-centred lattice there are two atoms per unit cell, viz. one in the centre of the cell and one made up of one eighth share in each of the eight corner atoms. The mass of an atom may be obtained by multiplying the atomic weight by the mass of the hydrogen atom. Thus, when the lattice constant of a given body-centred cubic metal has been obtained by X-ray analysis, its density may be determined by means of the equation:

$$\text{density} =$$

where m = mass of the hydrogen atom, i.e. 1.662×10^{-24} gm.

M = atomic weight of the metal

a = the lattice constant.

The face-centred cubic lattice described below is another type that is common in metal crystals. In this lattice there are four atoms per unit cell, and the density of face-centred metals can be calculated from the lattice constant by substituting 4 for 2 in the above equation. Owing to the fact that the determination of the lattice constant is independent of imperfections in the metal, and owing to the accuracy of modern data on atomic weights and the mass of the hydrogen atom, densities calculated in the above way approach more closely to the true densities of metals than those obtained by more direct methods.

Two more ways of packing spheres to imitate the arrangement of atoms in metal crystals are shown in Fig. 6. In the first layer, represented by full circles in the top portion of the figure, the atoms are placed so as to give the closest possible packing. The centres of the atoms thus arranged lie at the apices of equilateral triangles instead of at the corners

pointing downwards. Now the arrangement of the small circles in the middle portion is the same as that of the black dots, and they may be connected by lines similar to those shown connecting the first layer atoms in the top portion. When these are drawn, the small circles are situated at the apices of triangles and there are two alternative ways of placing the third layer of atoms. If these are placed so that their centres are over the centres of the triangles with apices pointing upwards then the atoms in the third layer overlie those in the first layer. Subsequent layers are thus a repetition of the first two and the general arrangement of the atoms in the lattice is represented in plan by the black dots and white circles. If, however, the atoms in the third layer are placed so that their centres are over the centres of the triangles with apices pointing downwards, then the centres of the atoms in the third layer are situated as shown by the crosses. The fourth layer overlies the first and the general arrangement of the atoms in the lattice is represented in plan by the dots, circles, and crosses.

The two arrangements described above are represented respectively on the right and left of the middle portion of Fig. 6. The atoms of zinc, magnesium, cadmium, and beryllium are arranged as shown on the right while those of copper, aluminium, lead, nickel, gold, silver, &c., are arranged as shown on the left. It now remains to describe how the centres of atoms arranged in these ways are connected up to form the unit cells of the space-lattices.

When points, e.g. atomic centres, are arranged in a regular pattern in space they may be connected together in numerous ways to form cells. The reasons which lead to the selection of one particular way of joining these points will be given later. Meanwhile, attention will be confined to explaining how the unit cells are derived from the arrangements represented in Fig. 6. The black dots representing the centres of the first layer atoms may be supposed to be situated at the centres and corners of hexagons as shown at the right-hand side of Fig. 6. The same applies to the small circles of the second layer and of course to all other layers which overlie these two. The unit cell is constructed by taking one hexagon from the first layer and a corresponding one from the third. Between these two hexagons three atoms in the second layer are enclosed, and the unit cell is as shown at the right-hand side of the bottom portion of Fig. 6. This is known as the close-packed hexagonal lattice. The three atoms in the middle of the unit cell are shared by no other cells. The atoms in the centres of the top and bottom faces are each shared by two cells, while each of the twelve corner atoms is shared by six cells. In the close-packed hexagonal lattice there are therefore six atoms per unit cell.

In deriving the unit cell to represent the arrangement in space of the centres of atoms disposed as indicated by the dots, circles, and crosses at the left-hand side of Fig. 6 the following method is adopted: The first layer lattice point O , the second layer lattice points P , Q , R , the third

layer lattice points L , M , N , and the fourth layer point G (which overlies O) form a cell as shown by the broken lines at the bottom left hand of Fig. 6. When several of these cells are drawn, however, it is seen that the numerous alternative ways of connecting the lattice points include the method indicated by the full lines. Thus, when atoms are packed as shown by the dots, circles, and crosses, their centres may be joined so that they are situated at the corners and in the centre of the faces of little cubes. This arrangement is known as the face-centred cubic lattice and the unit cell has lattice points at the corners and in the centre of

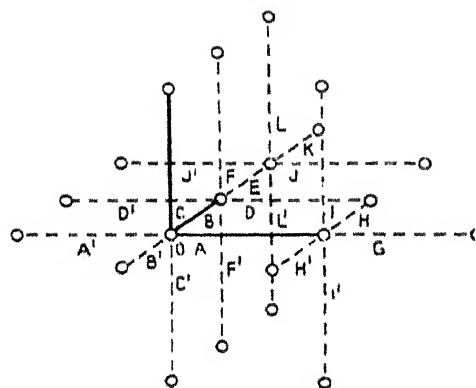


FIG. 7.

the faces as shown in the figure. As each corner atom is shared by eight cells and each face-centre atom by two cells, each unit cell contains four

General Description of Space-

The three arrangements of atoms described above are those that occur most frequently in the crystals of metals and alloys, but as other lattices which cannot

be by packing spheres are also formed, it is necessary to a more general account of them. A space lattice is a regular arrangement of points in space and this regularity can be described by stating that every point has neighbours in the same directions and at the same distances as every other point. Between 1835 and 1856 the problem of constructing space lattices was investigated by Bravais who adopted the following method. From a lattice point O three vectors A , B , C , and three reverse vectors A' , B' , C' , are drawn as shown in Fig. 7. The reverse vectors are continuations of and equal in length to the vectors, and the end points of the vectors and reverse vectors are lattice points. From each of these new lattice points a similar set of vectors is drawn as indicated by D , E , F , D' , E' , and F' , and the process is repeated at each of the new lattice points thus obtained. As the position of each lattice point in relation to its neighbours is determined by the lengths and directions of the vectors, each point has neighbours in the same directions and at the same distances. The arrangement of points thus obtained is therefore a space-lattice, and by varying the relative lengths of the vectors and the angles they make with each other different lattices may be constructed.

For any given arrangement of points in space there are numerous ways of connecting them so as to divide the space into cells. The Bravais vectors used in constructing a lattice divide space into cells and

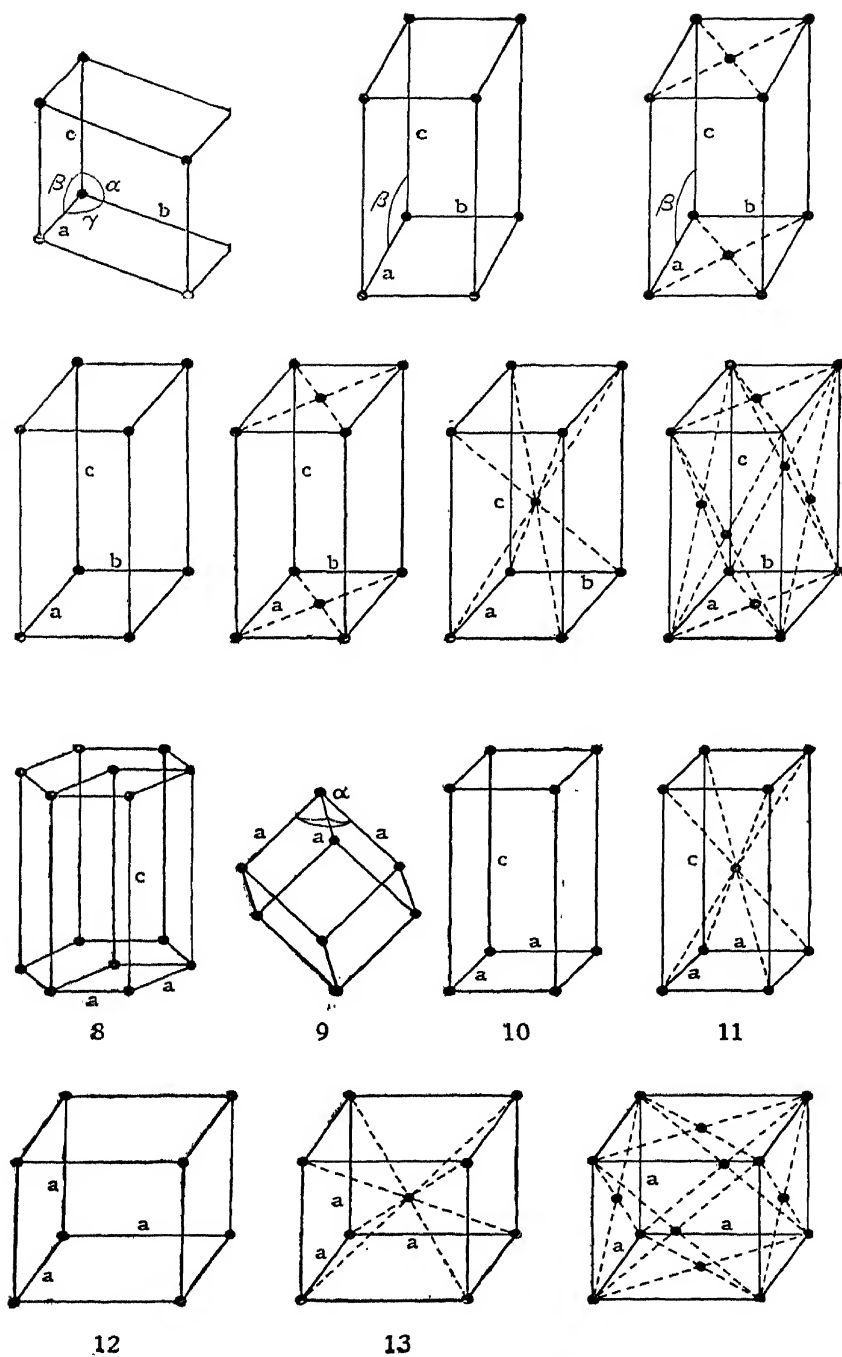


FIG. 8. Fourteen types of unit cell. (Bragg, *The Crystalline State*.)

the cells obtained in this way are so formed that each lattice point is situated where eight cells meet and no points are enclosed in the cells. There is thus one lattice point per cell. Before attention was devoted to a consideration of space-lattices, however, crystallographers had classified crystals into six systems on the basis of their symmetry as revealed in external forms. For each system they selected a set of axes to which the faces of the crystals could be related, and as space lattices can be classified into the same six systems it is customary to draw the unit cells so that their edges are related to the crystallographic axes of these systems. Thus the fourteen different space lattices that may be constructed by the Bravais method are represented by the unit cells shown in Fig. 8. The descriptions of the unit cells and the systems to which they belong are given in Table 6.

TABLE 6

Triclinic System.

Unit Cell. Three contiguous edges are all different lengths, a , b , c , and none are at right angles.

- (1) Simple lattice, with atom at each corner of cell.

Monoclinic System.

Unit Cell. Three contiguous edges are all different lengths a , b , c . One is at right angles to the other two which are not at right angles to each other.

- (2) Simple lattice with atom at each corner of unit cell.
- (3) End face-centred lattice.

Orthorhombic System.

Unit Cell. Three contiguous edges are all different lengths a , b , c , and are all at right angles.

- (4) Simple lattice with atom at each corner of unit cell.
- (5) End face-centred lattice.
- (6) Body-centred lattice.
- (7) Face-centred lattice.

Hexagonal System.

The axes of this system do not coincide with the edges of the unit cell. The crystals are related to four axes. Three are in one horizontal plane and make angles of 120° with each other. The fourth is vertical. The three horizontal axes are of the same length (a), the vertical axis is of a different length (c). Axial ratio is c/a .

Unit Cells.

- (8) (A) Hexagonal prism with one atom at each corner and in centre of each end face.
- (9) (B) Rhombohedron, with one atom at each corner.

Tetragonal System.

Unit Cell. Three contiguous edges are all at right angles. Two are of equal length (a), one is of different length (c). Axial ratio c/a .

- (10) Simple lattice, with atom at each corner of unit cell.
- (11) Body-centred lattice.

TABLE 6—*continued**Cubic System.*

Unit Cell. Three contiguous edges are all equal and at right angles.

(12) Simple lattice, with atom at each corner of unit cell.

(13) Body-centred lattice.

(14) Face-centred lattice.

In the triclinic, monoclinic, and orthorhombic systems the three sides of the unit cells are of different lengths denoted by a , b , and c . In the hexagonal prism and the tetragonal cells the sides are of two lengths denoted by a and c . In the rhombohedron and the cubic cells the sides are all of equal length denoted by a . In the triclinic system none of the contiguous edges meet at right angles, in the monoclinic two of them form a right angle, and in the orthorhombic, tetragonal, and cubic each pair of contiguous edges meet in a right angle. In the hexagonal prism the vertical edge is perpendicular to the plane of the others and these meet at 120° . In the rhombohedron the angle between each pair of the three edges that meet in a point is the same, but it is not a right angle. The unit cells 1, 2, 4, 10, and 12 contain one atom per cell; 3, 5, 6, 9, 11, and 13 contain two atoms per cell; 8 contains three atoms per cell; and 7 and 14 contain four atoms per cell.

The Types of Lattice formed by Pure Metals.

The types of space-lattice formed by thirty-seven elementary metals that exist in one form only are given in Table 7.

TABLE 7

*Type of Lattice formed by Pure Metals that exist in
One Form only*

Face-Centred Cubic

Ca, Sr, Ba, Ni, Cu, Nb, Rh, Pd, Ag, Ir, Pt, Au, Pb, Al, Th

Body-Centred Cubic

Li, Na, K, Rb, Cs, V, Mo, Ta, W

Hexagonal Close-Packed

Be, Mg, Ti, Zr, Os, Zn, Cd, Te

Rhombohedral Hexagonal

As, Sb, Bi.

Tetragonal

In.

Tetrahedral Cubic

Ge.

Several metals, viz. iron, cobalt, cerium, thallium, tin, manganese, and chromium can exist in more than one form. These metals are said to be polymorphic. Each type of lattice is stable over a certain range of temperature. Under certain conditions it may persist at temperatures

outside this range, but under equilibrium conditions the lattice when the metal passes out of the range in which this particular is stable. The lattice transformation is accompanied by thermal, volume, electrical, and other changes.

Iron forms a body-centred cubic lattice below 906°C ., a face-centred cubic lattice between 906° and $1,403^{\circ}\text{C}$., and a body-centred cubic lattice between $1,403^{\circ}\text{C}$. and the melting point ($1,537^{\circ}\text{C}$.). The length of the side of the body-centred unit cell at atmospheric temperature is 2.86 \AA . (i.e. Ångström units). As the metal is heated the lattice expands. At 906°C . it changes to the face-centred form, and as heating is continued this lattice expands. At $1,403^{\circ}\text{C}$. it reverts to the body-centred form which also expands with rise of temperature, and when the change in the lattice constant between atmospheric temperature and the melting-point is plotted against temperature, the line representing the expansion between $1,403^{\circ}$ and $1,537^{\circ}\text{C}$. is a continuation of that representing the expansion between 15° and 906°C . This suggests that the form of iron stable below 906°C . is identical with that stable above $1,403^{\circ}\text{C}$. and this inference is confirmed by the fact that when a sufficient amount of any of the elements Al, Cr, Mo, P, Si, Sn, W, or V is alloyed with iron the face-centred form disappears, the two body-centred forms are merged, and there is no evidence of any transition from one to the other. Body-centred iron below 906°C . is known as α -iron, face-centred iron between 906° and $1,403^{\circ}\text{C}$. as γ iron, and body-centred iron above $1,403^{\circ}\text{C}$. as δ -iron. The only distinction between α and δ iron is that in pure iron and some alloys they are stable in different ranges of temperature.

Cobalt forms a close-packed hexagonal lattice below 477°C . and a face-centred cubic lattice above it. Cerium and thallium also exist in face-centred cubic and close-packed hexagonal forms. Tin can exist in three forms. α -tin (usually known as grey tin) is stable below 18°C . and has a tetrahedral cubic (diamond) lattice (described below). β (or white) tin is stable between 18° and 161°C . and has a body-centred tetragonal lattice, while γ -tin stable between 161° and the melting-point has a hexagonal lattice. Manganese also exists in three forms and the α and β modifications have lattices that are much more complicated than those generally formed by pure metals. α manganese is stable below 742°C . and has a cubic lattice with 58 atoms in the unit cell. β -manganese is stable between 742° and $1,191^{\circ}\text{C}$. and has a cubic lattice with 20 atoms in the unit cell, while γ -manganese stable above $1,191^{\circ}\text{C}$. has a face-centred tetragonal lattice with 4 atoms in the unit cell. Chromium prepared under certain conditions exhibits a close-packed hexagonal lattice, but the metal as ordinarily prepared and used has a body-centred cubic lattice and undergoes no change in form during heating and cooling.

None of the metals crystallize in the triclinic, monoclinic, or orthorhombic forms. The cubic form is by far the most common and the

OF PURE METALS

close-packed hexagonal is the next in order of importance. In metal crystals the unit hexagonal cell is that shown in Fig. 6 and not that shown in Fig. 8. Otherwise all the unit cells characteristic of metal crystals are shown in Fig. 8 except the complicated unit cells of α - and β -manganese and the tetrahedral cubic structure formed by α -tin and germanium. This type of lattice consists of two interpenetrating face-centred cubic lattices represented respectively by the black and white circles in Fig. 9. The face-centred cube formed by the black circles is shown divided into eight smaller cubes. The white circles are situated in the centres of four of these small cubes and so arranged that they lie at the corners of a tetrahedron. The face-centred arrangement of the white circles is not very apparent in the figure, but the circle at the bottom left hand is situated at the corner of a cube and the other three occur in the centres of the faces that meet at that corner. If the face-centred cube formed by the white circles was moved in the direction BA by an amount equal to one quarter of the length of the cube diagonal, it would be superimposed on that formed by the black circles.

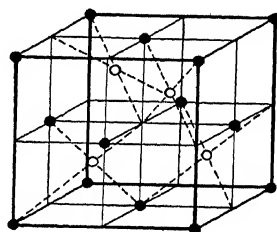


FIG. 9. Tetrahedral cubic lattice.

In Table 8 the dimensions of the unit cells of the lattices described in the foregoing are given.

TABLE 8

Lattices and Dimensions of Unit Cells

a = length of side of unit cube or rhombohedron.

a, c = lengths of sides of hexagonal prism or tetrahedral cell.

In Ångström units (1 Ångström unit = 10^{-8} cm.)

<i>Face-centred Cubic</i>				
<i>4 atoms per unit cell</i>				
Element	Ca	Sr	Ba	Ni
a	5.56	6.075	5.015	3.517
Element	Cu	Nb	Rh	Pd
a	3.608	3.294	3.820	3.882
Element	Ag	Ir	Pt	Au
a	4.0776	3.823	3.916	4.070
Element	Pb	Al	Th	γ -Fe
a	4.940	4.040	5.074	3.63 (1,100° C.)
Element	β -Ce	β -Co	β -Ti	
a	5.12	3.554	4.841	
<i>Body-centred Cubic</i>				
<i>2 atoms per unit cell</i>				
Element	Li	Na	K	Rb
a	3.460	4.30	5.200	5.62
Element	Cs	V	α -Cr	Mo
a	6.05	3.040	2.878	3.1401
Element	Ta	W	α -Fe	
a	3.296	3.159	2.821	

TABLE 8 *continued*
Hexagonal Close-packed
 6 atoms per unit cell

Element	Be	Mg	Ti	Zr
<i>a</i>	2.268	3.203	2.921	2.23
<i>c</i>	3.59	5.10	4.67	5.14
Element	Os	Zn	Al	Sn
<i>a</i>	2.724	2.659	2.873	3.450
<i>c</i>	4.314	4.935	5.606	5.520
Element	α -Co	β -Cr	α -Fe	Pb
<i>a</i>	3.65	2.717	2.514	4.41
<i>c</i>	5.01	4.418	4.105	5.912

Rhombohedral Hexagonal
 2 atoms per unit cell

Element	As	Sb	Bi
<i>a</i>	4.142	4.501	4.740

Tetragonal

<i>Face-centred</i> 4 atoms per unit cell		<i>Body-centred</i> 2 atoms per unit cell	
Element	In	Element	β -Sn
<i>a</i>	4.58	<i>a</i>	5.818
<i>c</i>	4.03	<i>c</i>	3.174

Tetrahedral Cubic
 8 atoms per unit cell

Element	Ge	α -Si
<i>a</i>	5.647	6.04

Manganese

α Cubic. 58 atoms per unit cell *a* = 8.894.

β Cubic. 20 atoms per unit cell *a* = 6.300 (20° C.).

γ Tetragonal. Face-centred *a* = 1.291 (extrapolated to 20° C.).

Crystallographic Planes.

The atoms in crystalline solids form a regular arrangement in space, and this regularity may be demonstrated by connecting the atomic centres with a system of imaginary lines that divide space into cells. It may also be demonstrated by drawing planes through the atomic centres. Any plane passing through a space-lattice is a crystallographic plane, and a series of parallel and equally spaced planes is a set of crystallographic planes. For the present purpose, however, a real set of crystallographic planes may be described as a series of planes passing through the atomic centres and so spaced that every atom is included on some plane in the series and every plane passes through some atomic centres. Thus, if Fig. 10 represents a plan of a body-centred cubic lattice in which cube-corner atoms are represented by black circles and cube-centre atoms by white circles, then the lines *AB*, *CD*, *EF*, &c., represent traces of one set of crystallographic planes and *WE*, *XI*, *YM*, &c., represent traces of another. *AB*, *EF*, *IJ*, &c., cannot be regarded as successive members of a real set, for such a set does not include planes passing through the atoms shown in planes *CD*, *GH*, *KL*,

&c. Furthermore, planes intermediate between AB and CD , CD and EF , &c., are not members of a real set because they do not pass through atomic centres.

If one particular plane is drawn through the atomic centres in a given lattice, then all planes parallel to it and passing through atomic centres are members of a set. The spacing of the planes in the set is determined by their direction in relation to the arrangement of the atoms in space. In Fig. 10 the traces of three sets of planes respectively parallel to AB , WE , and 12 are shown, and it is clear that the planes parallel to AB are less widely spaced than those parallel to WE and more widely spaced

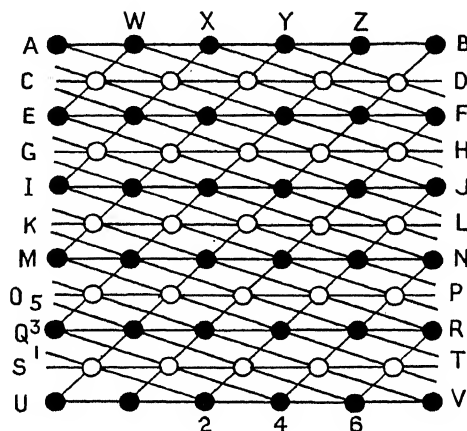


FIG. 10. Plan of body-centred cubic lattice, showing traces of crystallographic planes.

than those parallel to 12. Thus the spacing of the planes is determined by their direction relative to the arrangement of the atoms, and as the number of atoms in a given volume is constant, the atoms are most closely packed on the widely spaced planes and least closely packed on the closely spaced planes.

Numerous sets of planes may be drawn through the centres of a regular arrangement of atoms, and in order to distinguish one set from another, and to describe the relation of a given set of planes to the space-lattice, some method of denoting the position of planes is required. As planes passing through the lattice cut the edges of the unit cells their position in the lattice is given in terms of their intercepts on these edges. In the cubic system three contiguous edges of the unit cell are taken as axes and the position of planes is given by stating the number of parts into which a set divides these edges. At the top of Fig. 11 a set of planes in a simple cubic lattice is shown. a is the length of the edge of the unit cell. In the direction OA the distance between successive planes is $a/3$, in the direction OB it is $a/2$, and in the direction OC it is a . Thus the set of planes shown divides the edge of the unit cell into 3 parts in the

direction OA , into 2 parts in the direction OB , and into 1 part in the direction OC . This set of planes is therefore denoted by the index (321) which indicates the spacing of the planes and their position in the lattice. In the lower portion of Fig. 11 another set of planes is shown. This divides the edge of the unit cube into 1 part in the directions OA and OB , but being parallel to the edge of the cube in the direction OC it does not divide it. This set is therefore denoted by the index (110). Further examples of crystallographic planes are shown in Fig. 12. $OBFC$ and $AGED$ are successive members of a set that divides the edge

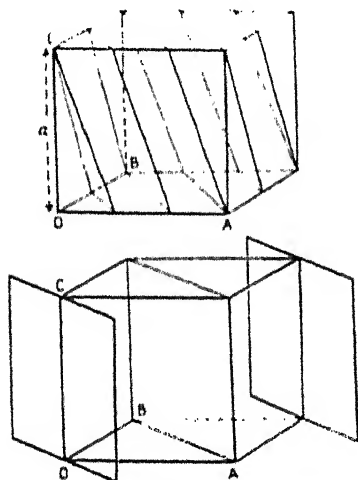


FIG. 11. (321) and (110) planes in cubic lattice.

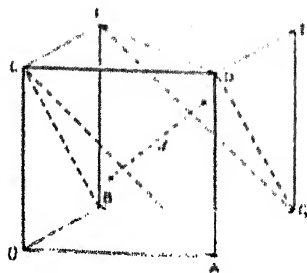


FIG. 12. Distance between successive (111) planes.

of the unit cell into 1 in the direction OA and into 0 in the directions OB and OC . They are therefore members of a set of (100) planes. CAB and $DGEF$ are successive members of a set that divides the edge of the unit cell into 1 part in the directions OA , OB , and OC , i.e. (111) planes.

$OADC$ and $BGEF$ (Fig. 12) are successive members of a set of planes that have the same spacing and the same relation to the lattice as the set that includes $OBFC$ and $AGED$. The same applies to the planes $CDEF$ and $OAGB$. Thus the three sets of planes parallel respectively to $OBFC$, $OADC$, and $OAGB$ are similar. They may be distinguished when necessary by designating them (100) (010) and (001) planes, but in general they are all called (100) planes. There are thus three sets of (100) planes, and similarly there are four sets of (111) planes parallel respectively to ABC , ABE , OGD , and OGF , and six sets of (110) planes parallel respectively to $ADFB$, $OGEC$, $OAEF$, $CDGB$, $DEBO$, and $CFGA$. In general the number of sets of planes denoted by an index is found from the following rules:

If all the indices are different and none are zero (say 123), there are 24 sets of similar planes.

If two indices are the same and none are zero (say 112), divide 24 by 2.

If three indices are the same (say 111), divide by 6.

If one index is zero (say 110), divide again by 2.

If two indices are zero (say 100), divide again by 4.

Thus the number of sets of planes that may be referred to generally as (112) planes = $24 \div 2 = 12$; the number that may be referred to generally as (120) planes = $24 \div 2 = 12$; while the number that may be referred to generally as 100 planes = $24 \div 2 \div 4 = 3$.

The Spacing of Crystallographic Planes.

In a simple cubic space-lattice the distance between successive (100) planes is equal to a , the length of the edge of the unit cube. The distance between successive (110) planes (Fig. 11) is equal to one-half the cube-face diagonal, i.e. $a/\sqrt{2}$, and the distance between successive (111) planes (Fig. 12) is equal to one-third of the cube diagonal, i.e. $a/\sqrt{3}$. In general the spacing of planes in any given set may be obtained from the formula

$$d(hkl) = \frac{a}{\sqrt{h^2 + k^2 + l^2}},$$

where d is the distance between successive planes in a set with the index (hkl) and a is the lattice constant. By substituting values of h , k , and l in the above equation the relative spacing of the planes in different sets may be ascertained, and if a is known, the absolute spacing may be calculated. The planes may then be set down in the order of their spacing, viz. (100) (110) (111) (200) (210) (211) (220) (221) (300) (310) (311) (222) (320) (321) (400) (410) (322) (411) (330) (331), &c. The most widely spaced planes are those with the simplest indices such as (100) (110) and (111). They are also the most important in that they form the most commonly occurring faces on perfectly developed crystals, give rise to the most important X-ray reflections, and are the planes along which slip takes place when metal crystals are deformed.

Any values of h , k , and l may be substituted in the above equation and the relative or absolute spacing of the corresponding planes obtained. But all the spacings thus calculated do not apply to sets of planes so spaced that every atom is situated on some member of the set and every plane passes through some atomic centres. In the simple cubic lattice every member of a set of planes with an index that contains 1 passes through atomic centres, and every possible set of planes includes all the atoms. The same does not apply to the face-centred and body-centred lattices, and these must now be considered.

Fig. 13 is a unit face-centred cube. BED and CFH are successive members of a set of (111) planes other members of which pass through A and G respectively. Thus all the atoms in the unit cell lie on this set of planes. $ADHE$ and $BCGF$ are successive members of a set of (100) planes and the face-centre atoms J , O , L , N are not situated on either of them. A real set of planes should include these atoms, therefore

the plane $PQRS$ must be added to the set. $ADHE$, $PQRS$, and $BCGF$ are successive members of a set for which the index is (200). Thus in the face-centred lattice there are (200) instead of (100) planes. $BFHD$ is one of a set of (110) planes other members of which pass through GC' and EA respectively. The face-centre atoms J , M , K , L are not situated on planes in this set and to include them the spacing of the planes must be reduced to (220). Fig. 14 is a unit body centred cube. The cube-centre atom J lies on the same (110) plane as the corner atoms $BFHD$ and this holds generally for (110) planes. In the case of (100) and (111) planes, however, the cube-centre atom does not lie on planes through

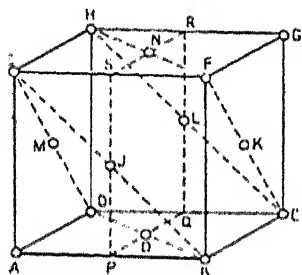


FIG. 13.

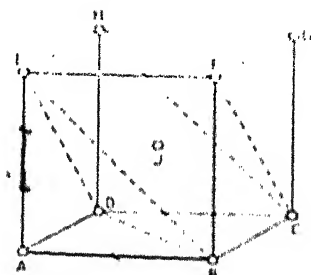


FIG. 14.

the corner atoms. In order to include it the spacings must be to (200) and (222) respectively.

A set of planes that divides AB (Fig. 13) into h parts and AE into k parts divides the face diagonal AF into $h + k$ parts. If $h + k$ is even, one of the planes will pass through J ; if it is odd, J will be situated between the planes. Similarly, M will lie on one of the planes of a set that divides AE into k parts and AD into l parts if $k + l$ is even, and O will lie on one of the planes of a set that divides AB into h parts and into l parts if $h + l$ is even. In general, therefore, the indices of planes pass through corner and face-centre atoms are such that the of $h + k$, $k + l$, and $l + h$ are all even, i.e. h , k , and l are all odd or all even. A set of planes that divides AB (Fig. 14) into h parts, AE into k parts, and AD into l parts divides the cube diagonal AG into $h + k + l$ parts. If $h + k + l$ is even, one of the planes will pass through the body-centred atom J , and in general the indices of planes that pass through corner and body-centre atoms are such that $h + k + l$ is even.

The above rules give the indices for sets of planes that include all the atoms, and so long as the index of a set is not a multiple of that of another set, every plane passes through some lattice points. It is now possible to tabulate the spacing of the most important planes in the cubic lattices in terms of the lattice constant a . In the first place, the spacing d of possible planes is calculated from the equation

$$d(hkl) = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

The indices of these planes are then set down in the order of spacing as shown in the first column of Table 9. Taking account of the above rules the spacings of the planes that pass through atomic centres and include all atoms are then entered in the second, third, and fourth columns. From this table it will be seen that the order of spacing is (100) (110) (111) (210) (211) (221) (310) (311) in the simple cubic, (111) (200) (220) (311) in the face-centred, and (110) (200) (211) (310) (222) in the body-centred.

TABLE 9
Spacing of Planes in Cubic Lattices

<i>Planes</i>	<i>Simple cubic</i>	<i>Face-centred</i>	<i>Body-centred</i>
100	1.000
110	0.707	..	0.707
111	0.577	0.577	..
200	..	0.500	0.500
210	0.447
211	0.408	..	0.408
220	..	0.354	..
221	0.333
300
310	0.316	..	0.316
311	0.301	0.301	..
222	0.288

In the foregoing discussion of crystallographic planes attention has been confined to sets so drawn that all the lattice points lie on some member of the set and every member of the set passes through lattice points. The spacing of such sets of planes is determined by their position in the lattice. There are, however, numerous sets of planes in which only some members pass through lattice points, e.g. 200, 220, 300, 320, 400, &c., in the simple cubic lattice. There are also numerous sets that do not include all the lattice points, e.g. 100, 110, 210, 211, &c., in the face-centred lattice. In general all these planes are regarded as crystallographic planes. Furthermore, in the foregoing both the spacing and the direction of the planes have been taken into account, but for most purposes it is only the direction that matters. Thus it is not usual to refer to the (200) or (220) planes in the face-centred or the (200) (222) planes in the body-centred lattice. These have the same directions relative to the lattice as the planes with twice their spacing, i.e. (100) (110) and (111). It is customary therefore to refer to the (100) (110) and (111) planes in the face-centred and body-centred cubic lattice, thus giving their direction relative to the lattice, and to denote their spacing by stating that (100) and (110) planes in the face-centred and (100) and (111) in the body-centred have half the spacing of corresponding planes in a simple cubic lattice of the same size.

Crystallographic Directions.

A line passing through atomic centres is a crystallographic direction and its position in the lattice is given by an index $[uvw]$ enclosed in

square brackets. OA , OB , and OC (Fig. 15) are contiguous edges of a unit cell of length a . A direction represented by an index $[uvw]$ is obtained as follows: Beginning at O a length equal to $u \cdot a$ is measured along OA , from the point thus reached a length equal to $v \cdot a$ is measured parallel to OB , and from the point thus reached a length equal to $w \cdot a$ is measured parallel to OC . The line joining this last point to O is the crystallographic direction $[uvw]$. OA (Fig. 15) is a $[100]$ direction, OB is a $[010]$ direction, and OC is a $[001]$ direction. As these have similar positions relative to the lattice they are all usually referred to as $[100]$ directions. OP (Fig. 15) is a $[110]$ direction, OF a $[111]$ direction, and OH a $[102]$ direction. There are six $[110]$ directions and four $[111]$ directions, and in general the number of directions corresponding to a

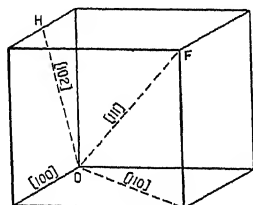


FIG. 15.

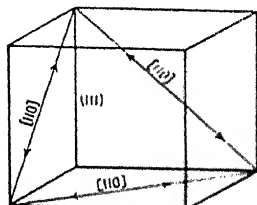


FIG. 16.

given index is the same as the number of planes corresponding to a similar index, e.g. there are twelve sets of (112) planes and twelve $[112]$ directions. Furthermore, a line representing a given direction is normal to a plane with a similar index, e.g. a $[111]$ direction is normal to a (111) plane and a $[112]$ direction is normal to a (112) plane.

Direction lines lie in certain planes. Thus the $[111]$ direction in Fig. 15 lies in the (110) planes $FGOA$, $FCOP$, and the $[110]$ direction lies in the (100) plane $APBO$ and the (110) plane $OPFC$. In a given (111) plane there are three $[110]$ directions, in a given (100) plane there are three $[100]$ and two $[110]$ directions. The $[110]$ directions in a (111) plane are shown in Fig. 16, and when a metal crystal is said to deform by slipping on (111) planes in a $[110]$ direction, it means that movement of one part of the crystal with respect to another takes place by gliding along a group of (111) planes in one of the six directions indicated by arrows in Fig. 16.

Orientation.

The orientation of a crystal is the relation of its lattice to any fixed system of planes. All the crystals in a group have the same orientation when their corresponding planes are parallel, they have a random orientation when there is no relation whatever between their planes, and they have a common direction when a corresponding crystallographic direction in each crystal is parallel to a given line. A specimen of

a pure metal is composed of crystals each of which consist of the atoms of that metal arranged in the space-lattice characteristic of it. Apart from variations in their size and shape there is nothing to distinguish one crystal from another when they are considered individually. But when the group of crystals of which the metal is composed is considered as a whole the crystals are distinguished by their orientation. One may have a set of (100) planes parallel to a particular surface of the specimen, another may have (111) planes parallel to this surface, another may have (110) planes parallel to this surface, and so on through all the possible planes. When this condition is realized, the crystals in the metal are oriented at random and this is its normal state. After certain treatments, however, all the crystals in a specimen may have one direction parallel to a given line. They are then said to have adopted a preferred orientation.

Orientation is important because the properties of crystals are to some extent directional. Thus, if a series of wires each consisting of one crystal of a given metal is prepared, and if the orientation of the crystals with respect to the axis of the wire varies from specimen to specimen, then certain properties measured in the direction of the wire axis will also vary from specimen to specimen. If, e.g., the wires are subjected to a tensile pull until they break, the amount of extension that takes place before fracture and the force required to produce it will vary. Similarly, the magnetic properties measured in the direction of the wire axis will vary with the orientation of the crystal composing it, and so will the electrical conductivity if the crystals concerned are not cubic. Single metal crystals exhibit directional properties as do samples of metal in which a preferred orientation exists, but those containing numerous crystals oriented at random have no such properties, because the directional attributes of the individual crystals cancel out in the aggregate.

✓ FURTHER CONSIDERATION OF THE MICROSTRUCTURE OF PURE METALS

With the exception of tungsten and molybdenum which are prepared by compressing a metal powder obtained by reducing the oxide, and certain metals that are extracted or refined by electro-deposition and not subsequently melted, metals are molten at the end of the manufacturing operations. They are then poured into moulds to solidify. This is a complicated process and will be fully considered at a later stage. Meanwhile a simplified description may be given. If it is supposed that the temperature is uniform throughout the molten mass, then, when it has cooled to the requisite temperature, numerous small crystals will appear. These are crystal nuclei and their distribution throughout the mass is determined by probability. From each of these a crystal grows and the heat evolved during the process tends to maintain constant and

even to raise the temperature of the mass. The appearance of the first generation of nuclei does not, however, conclude this stage of the process, and unless they were very close together fresh ones will appear while crystallization from others is going on. These later nuclei tend to appear at points remote from the original ones and thus a fairly uniform distribution results.

From each nucleus a crystal grows and the rate of growth in the absence of interference will be the same for each crystal. This continues until the liquid has solidified and contact between the separate crystals has been established. As all metals except bismuth and some varieties of cast-iron contract on passing from the liquid to the solid state, and as this contraction takes place at the surface of the growing crystals, it is evident that the disappearance of the liquid will only coincide with the establishment of complete contact between the crystals when there is a free flow of liquid into the interstices between them. If this condition is perfectly satisfied, all the contraction will be concentrated in a cavity formed on the top of the metal. But in practice, when solidification is nearly complete, the liquid does not flow into all the interstices between the crystals, and in consequence small cavities remain. These, however, may be neglected for the time being.

The number of crystals in a given volume (i.e. the average crystal size) depends on the number of nuclei formed. Their shape depends on the form they assume while growing freely and the contacts they make with their neighbours. Although the points at which nuclei appear are not uniformly distributed, the crystals finally formed are all about the same size. This is due to the fact that the position of a crystal is not fixed until it makes contact with those around it. Where several crystals are growing from closely spaced nuclei contact will soon be established, but unless a crystal is entirely surrounded by neighbours its growth may still continue in certain directions. Thus the fact that the original nuclei are not uniformly distributed throughout the mass is to some extent counterbalanced by the fact that all the crystals grow at about the same rate.

In metals that do not undergo polymorphic changes, i.e. pass from one type of space-lattice to another, the crystals formed at solidification remain unchanged at atmospheric temperature unless the metal is deformed. Furthermore, in such a case the structure formed originally may be heated and cooled without change. In a pure metal this consists of crystals approximately similar in size and shape and composed of the same atoms arranged in the same space-lattice. There is, however, no relation between the orientations of the individual crystals, and it is because of this that one crystal may be distinguished from another.

Crystal Boundaries.

To complete the description of the structure of a pure metal it is necessary to consider how the individual crystals are joined together,

i.e. the nature of the crystal boundaries. The ideal case is that of the boundaries between the constituent crystals of an absolutely pure metal, and it is this with which we are now concerned. There is, however, so little definite knowledge about crystal boundaries that it is not possible to discuss the points of similarity and difference between the different cases provided by boundaries (1) between similar crystals of (a) pure metals, (b) solid solutions, and (c) other constituents of alloys, or (2) between different kinds of crystals. Thus while the following discussion applies particularly to the boundaries between adjacent crystals in a pure metal it may also be said to apply generally to all types of boundaries.

When impurities or added elements are present in a metal they frequently form films or envelopes round the crystals of the basis metal. These films are sometimes accepted as the crystal boundaries, and it is assumed that they act as a cement between the crystals and account for the cohesion between them. It is true that these films cement the crystals together, but the actual boundaries are the surfaces of contact between these films and the crystals on each side. Thus the existence of boundary films of another phase does not account for the cohesion between crystals, for this can exist in the absence of such films which actually introduce two boundaries between different phases in place of one boundary between different crystals of the same phase.

The crystal boundaries now under consideration are the surfaces of contact and cohesion between adjacent crystals of different orientations or different kinds, and the problem is to discover how the conditions at, or in the vicinity of boundaries, differ from those in the interior of crystals. This is a subject on which there is no direct experimental evidence, for the boundaries themselves are abstract rather than material, and the dimensions of the regions near the boundaries which are affected by the boundary conditions are negligible in comparison with those of the crystals as a whole. As a consequence of this, ideas about boundary conditions are essentially speculative and are based either on particular interpretations of the behaviour of crystal aggregates, or on theoretical consideration of what is likely to occur where two crystals meet. Much has been written about boundaries, and the history of the subject has recently been reviewed by Bucknall (6), but no purpose would be served by considering this fully here and a few comments must suffice.

In considering the development of hypotheses about crystal boundaries from observation of the behaviour of crystal aggregates three aspects of the subject may be distinguished. In the first place, there is the separation of the effects attributable to the boundaries from those attributable to the crystals. Secondly, there is the process of inferring from the effects attributable to the boundaries something about their nature, and, thirdly, there is the application of tests to discover whether the resulting hypothesis actually explains what it purports to. Most of

what has been written about crystal boundaries fails to withstand critical examination from these points of view, and when it is carefully considered, it becomes apparent that the main object was to find an easy way of explaining the behaviour of metals by attributing certain properties to the boundaries. The behaviour of metals when subjected to stress under different conditions of time and temperature has been the principal basis of speculation about the nature of crystal boundaries. It is found, for example, that the resistance to deformation of a metal increases as the size of the constituent crystals decreases, and, when a metal is fractured at atmospheric temperature, the rupture passes through the crystals rather than along the boundaries. It was deduced from this that the boundaries are stronger than the crystals. As the temperature is raised, however, the tendency for fracture to take place at the boundaries increases, and it was deduced from this that the boundaries lose strength on heating more rapidly than the crystals. Having concluded that the boundaries were stronger than the crystals at atmospheric temperature, and lost strength more rapidly on heating, it was assumed that these characteristics of the boundaries could be accounted for by postulating that the crystals in an aggregate were held together by means of an amorphous cement, i.e., a film not necessarily of different composition from the crystals but distinguished from them by being without a definite crystal structure. This was the basis of the amorphous hypothesis as applied to crystal boundaries, and for a full account of its development, of the different interpretations put on the word, and of the different characteristics attributed to amorphous material the above-mentioned review by Bucknall or the books by Jeffries and Archer (17) or Rosenhain (8) should be consulted. For the present it will be enough to say that the hypothesis was generally if not universally accepted for a long time and that even now it is not without its advocates.

In Chapters III and IV the behaviour of metals when subjected to stress under different conditions of time and temperature is dealt with at some length, and it is shown (1) that the increase in resistance to deformation which accompanies a decrease in crystal size may be accounted for on the basis of the established fact that there is a difference in orientation between the adjacent crystals in an aggregate, (2) that at atmospheric temperature fracture takes place through the crystals because of certain changes that are produced in them by the deformation that precedes fracture, and (3) that intercrystalline fracture is the result of a combination of several factors, but is mainly due to the fact that at elevated temperatures the changes mentioned under (2) do not occur. Thus as a result of the more careful consideration that has recently been given to the mechanical behaviour of metals it is possible to account for it without supposing the existence of two phases, a crystalline and an amorphous. Even if the necessity of postulating the existence of a boundary cement with different proper-

ties from the crystals is admitted, the evidence obtained from the study of mechanical behaviour does not throw any light on the nature of this cement, for the argument that boundaries are stronger than crystals, and amorphous material stronger than crystalline, therefore crystal boundaries are amorphous, is not convincing. In any case the main object of the amorphous boundary hypothesis was to account for certain aspects of the mechanical behaviour of metals, and it was not a serious attempt to solve the problem of the conditions that exist at the surfaces of contact and cohesion between different crystals. It introduced the idea of a cementing film, but ignored the fact that if cohesion between one crystal and another could not be accounted for without assuming an intervening film, how then could cohesion between this film and the crystals be explained?

There is actually a considerable amount of evidence which indicates that in the regions near the boundaries the properties of crystals are different from those at points more remote, and this conclusion may also be arrived at by considering what is likely to happen where crystals of different orientation meet. The nature of the forces that bind the atoms together in crystals is considered in a later section, and it may be said that the forces that bind the crystals together are fundamentally the same. Atoms in the interior of crystals are surrounded, however, by a particular number of immediate neighbours situated at certain distances and in certain directions, and these neighbours are in turn surrounded by a similar number of similarly disposed neighbours. Atoms at the surface of contact between different crystals are differently situated, for they are connected on the one hand to a lattice oriented in one way and on the other to a lattice oriented in a different way. They may have more or fewer immediate neighbours situated at different distances and in different directions from those that prevail in the interior of the crystals. It is therefore to be expected that the lattice at the boundary will be to some extent distorted and that the binding forces will not be utilized in the normal way. Furthermore, as the atoms at the actual boundary are in turn the neighbours of those adjacent to the boundaries, these latter will also be differently situated from atoms in the interior of the crystals, and between two crystals there is therefore a boundary zone in which the distortion varies from zero to a maximum and to zero again as the arrangement of the atoms changes over from that of one crystal to that of the next. Thus, in the absence of impurities or cavities at the boundaries, a solid metal may be regarded as an assemblage of crystals connected by distorted zones or as a crystalline mass in which the orientation changes at certain points; the change being accomplished gradually over a small distance by the displacement of atoms from their ideal positions. This is practically all that can definitely be said about crystal boundaries, but it is sufficient to account for what is at present known about their characteristics. Thus it is known that when other elements are diffusing into a metal this diffusion sometimes

takes place preferentially along the crystal boundaries as explained in Chapter VI. It is also known that diffusion takes place more rapidly through crystals that have been distorted by mechanical deformation than through more stable crystals, and it may therefore be inferred that the lattice is distorted near the boundaries. Furthermore, it is known that when a new phase is forming in a solid metal, it tends to appear in the first instance at crystal boundaries or in regions of the crystals that have been distorted by cold work. This and other evidence which will be considered in different parts of this book, goes to show that in the boundary zones the crystal lattice is distorted and less stable than elsewhere, but it does not enable this distortion or instability to be more precisely defined. It appears in general that the conditions at the boundaries between crystals are intermediate between those that prevail in the interior of crystals and those that prevail at the surfaces of metals, and consequently the final section of this chapter is not without significance from the present point of view.

✓ THE MICROSCOPIC EXAMINATION OF METALS

Microscopic examination is the most important and most widely employed method of studying solid metals and more than any other it provides a picture of a metal as an aggregate of crystals. By means of the microscope the size and shape of the crystals in a given sample of pure metal may be studied. In alloys that consist entirely of one kind of crystals variations in the distribution of the constituent elements in the individual crystals may be seen, as may the relative amounts and distribution with respect to each other of the different kinds of crystals in alloys that contain more than one kind. In the various branches of natural science in which the microscope is used as an instrument of investigation the specimens are sufficiently transparent to be examined by transmitted light. Metals, however, are opaque substances and must be examined by reflected light. Consequently, the metallurgical microscope and general technique of an examination are different from those of other sciences. A full description of the special apparatus and methods required is contained in various books on metallography (7, 8, and 9).

For the examination of metal specimens the surface must be illuminated in such a way that light is reflected from it into the objective of the microscope. This can be accomplished either by oblique or vertical illumination. In oblique illumination a beam of light is made to impinge on the surface of the metal as shown in Fig. 17. From all those parts of the specimen that are truly plane the incident rays of light I , I are reflected as shown by the rays R , R . Irregularities on the surface, however, will cause the incident rays to be reflected in numerous directions. In some cases the angle may be such that the whole of the ray is reflected vertically and passes into the objective. Such rays are shown at V , V . In other cases the angle of incidence is such that only

a part of the light is reflected into the objective. Such areas will therefore appear only partially illuminated.

Oblique illumination has the disadvantage that most of the incident light is usually reflected away from the objective and is therefore lost, and the appearance of the specimen illuminated in this way is difficult to interpret. This method, valuable though it is, is therefore used for special purposes only, and specimens are generally examined under vertical illumination. To obtain this the light must first pass through the objective to the specimen, next be reflected from the specimen back into the objective, and thence to the eyepiece. One method of illumination is shown in Fig. 18. The light coming from the source *S* passes

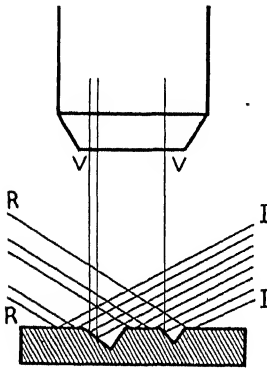


FIG. 17.

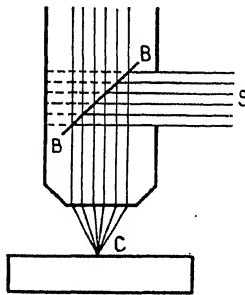


FIG. 18.

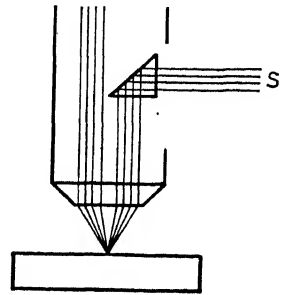


FIG. 19.

through a hole in the microscope tube and strikes the thin glass plate *B, B*, which is fixed at an angle of 45° to the optical axis of the microscope. Some of the light is reflected by this plate and passes downwards through the objective and on to the specimen at *C*. From this it is reflected and passes again through the objective and glass plate to the eyepiece. In this system of illumination light is lost at two stages. Only a portion of that which comes from the source is reflected downwards by the glass plate, the remainder passes through the plate and is lost. After reflection from the specimen some of the light passing up the microscope tube is reflected back towards the source by the glass plate, and only the remainder reaches the eyepiece. Nevertheless, the glass plate is superior in one important respect to the prism described below, since the whole of the objective is used for both incident and reflected light, and there is accordingly less danger of distortion of the image.

The prism illuminator is illustrated in Fig. 19. The light from the source is totally reflected by a right-angled prism and passes through one half of the objective. After reflection by the specimen it passes through the other half of the objective, behind the prism, and thence to the eyepiece. In this method the incident light is not quite vertical, and only half the objective is used in the microscopic examination. But the

image obtained is much brighter than when a glass plate is used, and mainly for this reason the prism illuminator is the one most generally employed. When vertical illumination is used, the light which strikes plane areas on the specimen is reflected back up the microscope tube, whereas that which falls on surface irregularities is to a greater or less extent reflected outside the objective. Plane surfaces therefore appear bright and irregularities more or less dark when viewed by this method.

In preparing metal specimens for microscopic examination the principal object is to produce a surface on which the plane areas and irregularities are related to the structure of the metal. The first stage is to prepare a level surface, and the second to produce irregularities on it. It is sometimes necessary to examine articles such as girders, shafts, tools, &c., without injuring them, but usually the examination is carried out on small specimens cut from the article concerned. Frequently the size is determined by circumstances, but in the absence of this, it is convenient if the surface to be examined is about one inch in diameter and the thickness about 0.5 inch. Very small or thin specimens such as wires or razor blades must be set in white metal or some kind of cement, the methods employed for doing which are described in the books already mentioned. After the specimen has been shaped the next operation is to make a flat surface, and this can be done by filing or grinding on a wheel, a Linisher, or a piece of emery-cloth. The pressure to be applied in doing this depends on the metal. If this is hard, some degree of pressure will be necessary, but soft metals should be filed or ground very gently, otherwise the structure below the surface will be distorted. Unless it is known that the metal will not be affected by heat, specimens should not be allowed to get warm during grinding or subsequent polishing. When preparing metals like quenched steel, grinding should be done under water and polishing on emery should be done under paraffin.

After it has been made flat, the surface to be examined is ground on graded French emery-papers, the ones most commonly used being numbered from the coarsest to the finest, 1, 0, 00, 000. The specimen is first rubbed on No. 1 paper until all the scratches produced by rougher paper or files are removed. It is then turned through a right angle and rubbed on No. 0 until all the scratches left by No. 1 have disappeared, and so on until the finest paper is reached. The object of grinding on the graded emery-papers is to gradually reduce the size and depth of the surface irregularities until they are small enough to be removed by the final polishing operation. If the specimen is not turned through a right angle between each successive paper, the scratches left by the previous paper will seem to have been eliminated before they really are. Polishing is performed by means of fine oxide powders, e.g. alumina, magnesia, or rouge, on a wet cloth, usually that sold specially for polishing under the name of 'selvyt'. This operation differs from the cutting action of the emeries designed to produce successively finer

scratches. By its means the very fine ridges left by the last emery-paper are bent over and worked into the grooves, and the surface of the metal is made absolutely smooth by plastic working.

Certain features of the structure of metals can be, and when present should be, observed by examining the polished surface. If the metal contains small cracks, blowholes, or other cavities, these may be studied, as also may any non-metallic substances, e.g., graphite in cast iron, slag in wrought iron, and sulphide inclusions in steel. Differently coloured constituents may also be recognized, and when there is a marked difference in the hardness of constituents, the hardest will be seen standing in relief. For the examination of the structure as a whole, however, the surface must be etched. Etching consists essentially in attacking the polished surface of the metal with a reagent that dissolves it slowly or deposits a film of some kind on some or all of the constituents. Many

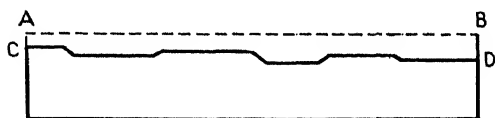


FIG. 20.

different methods have been devised for use with different metals and alloys, and for detecting small differences in the composition of certain constituents. A full list of reagents used in steel metallurgy is given in the *Metals Handbook* (15), while etching in general is dealt with by Berglund (16). Some of the reagents most frequently used are given in Table 10.

The first action of the etching reagent is to dissolve the thin layer of worked metal produced by grinding and polishing. It then attacks the undeformed crystals beneath. If the specimen is a pure metal, etching depends on the different orientations of the crystals. The surface to be examined is a section cut at random through an aggregate of crystals oriented in many directions and presenting different planes to the attack of the reagent. The rate at which the crystals dissolve varies according to the plane exposed. Thus by its means some crystals are dissolved to a greater extent than others and differences in level are produced. This is illustrated in Fig. 20 in which *AB* represents the original polished surface and *CD* the etched surface on which the boundaries of the crystals are marked by small steps. If these were quite vertical and if the illumination was also vertical, they would not be seen under the microscope, but they are actually slopes and the incident rays are not exactly vertical. Consequently, while the light striking the surface of the crystals is reflected through the objective as shown in Fig. 19 that which meets the boundary steps is reflected outside it. Under the microscope, therefore, the crystals appear as bright plane surfaces and the boundaries as black lines.

TABLE 10

Common Etching Reagents

<i>Reagent</i>	<i>Application</i>
1% Nitric acid in alcohol.	For revealing the m
2% " " "	pure iron, ordinary varieties of cast-
5% " " "	iron, and ordinary varieties of steel in
5% Picric " "	all conditions of heat-treatment.
	1% of nitric is probably best.
2 gm. picric acid; 25 gm. sodium hydroxide; water to make 100 c.c.	Sodium picrate; used boiling.
	ementite and other carbides
	in
1 gm. cupric chloride; 4 gm. magnesium chloride; 1 c.c. conc. hydrochloric acid; 20 c.c. water; 100 c.c. alcohol.	reagent. For showing
40 c.c. conc. hydrochloric acid; } 30 c.c. water; 5 gm. cupric chloride; } 25 c.c. alcohol. }	of phosphorus, &c., in
3 parts hydrochloric acid; 1 part nitric acid. }	solid solution in iron.
Saturated solution of ferric chloride in hydrochloric acid plus a little nitric. }	reagent. To reveal
Equal parts of strong ammonia and 3% hydrogen peroxide.	in :
Copper ammonium chloride 5 gm.; water 120 c.c.	<i>Aqua regia</i> . For structure of stain-
10% solution of ammonium persulphate in water.	less :
10 gm. ferric chloride; 120 c.c. water. }	For structure o steel.
Concentrated hydrochloric acid. }	For copper, brass, bronze, and
50 c.c. conc. nitric acid; 50 c.c. glacial acetic acid. }	aluminium bronze.
10% ammonium persulphate. }	For brass, bronze, aluminium
<i>Aqua regia</i> in glycerine. }	bronze.
1 part nitric acid; 1 part hydrofluoric acid; 3 parts glycerine. }	For nickel.
Hydrochloric acid (conc.). }	For nickel and copper-nickel alloys.
10 gm. chromic anhydride; 1.5 gm. sodium sulphate; 100 c.c. water. }	Copper reagents may also be used.
	For nickel-chromium alloys.
	For aluminium and its alloys.
	For lead, tin, antimony, bismuth, and their alloys.
	For zinc and its alloys.

The pure iron shown in Fig. 3 was etched with 1 per cent. nitric acid in alcohol, and the structure is revealed by the differences in level produced between the crystals. By etching for a longer time, in stronger solution or in a warm solution, the crystals may be further distinguished by a difference in colour. Iron is not usually treated in this way, but

other metals are usually etched so as to produce differently coloured crystals like those shown in Fig. 4. It is necessary to explain how differences in colour may result on different crystals of the same metal. Usually these are due to the production of oriented irregularities on their surfaces. When a smooth surface of a crystal is exposed to the action of an etching reagent it does not dissolve uniformly. The reagent penetrates along certain planes and produces a surface pattern which varies with the orientation of the crystal. On a given metal some

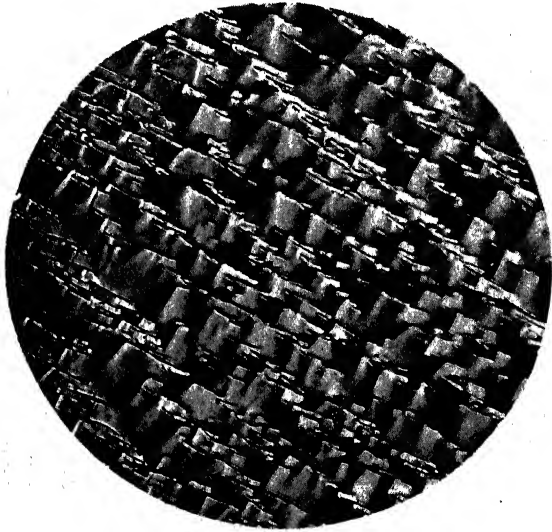


FIG. 21. Copper. Etched with molybdic acid and ammonia. $\times 500$.
(R. E. Richardson.)

reagents are more effective than others, and usually the pattern becomes more pronounced as the strength of the reagent is increased or the time of etching prolonged. Fig. 21 magnified 500 diameters shows the pattern produced on a crystal of copper by etching in molybdic acid and ammonia. Fig 22 at the same magnification reveals the structure of a crystal of tin etched in acid ferric chloride solution. These micrographs were kindly given to the authors by R. E. Richardson. Now when a pattern of this kind has been produced on the surface of a crystal it no longer reflects all the light back into the objective. The amount actually reflected depends on the orientation of the surface pattern in relation to the incident light. On a surface composed of a number of sections through differently oriented crystals the amount of light reflected into the objective varies from crystal to crystal. In any one position of the specimen some crystals appear light and others dark, but if the specimen is rotated under the microscope the tints alter and

crystals change from light to dark and vice versa during rotation. Many samples of metal contain crystals large enough to be seen by the naked eye, and when they are suitably etched, the play of tints produced by rotation is readily observed. To produce effects visible to the naked eye the etching must be deep enough to form microscopically visible surface patterns, but differences in colour seen under the microscope may be due to surface markings too fine to be resolved.

Another way in which differences in colour may be produced on the



FIG. 22. Tin. Etched with acid ferric
(R. E. Richardson.)

500.

crystals of a pure metal is by the formation of transparent oxide films of different thicknesses. When such a film is formed, light is reflected from the surface of the metal and the surface of the film. When the thickness of the film is equal to one half the wave-length of light of a particular colour, this colour is cut out of the reflections. Thus, if films of different thicknesses are produced on crystals of different orientation, these will appear differently under the microscope. Finally, differences in colour or tint may be caused by the formation on the surface of the crystals of a layer of some compound produced in the reaction between the metal and the etching reagent.

Homogeneous alloys, in which all the atoms present are uniformly distributed in the crystals, etch in the same way as pure metals. When the composition varies from point to point in the individual crystals, or when more than one constituent is present, then different constituents, or areas of different composition in the same constituent, are distinguished by an intrinsic difference in colour or hardness, by a difference

phenomena under consideration. The evidence in support of a secondary or mosaic structure is, accordingly, far from conclusive, and in this book it will not be regarded as an essential characteristic of crystals.

ATOMS, ELEMENTS, IONS, MOLECULES, CRYSTALS

In order to simplify the description of crystal structure atoms have so far been regarded as compact spheres and crystals as built up by packing them together. Actually, however, atoms are not compact spheres and crystal structure involves more than packing. Before proceeding further it is therefore necessary to outline a picture of crystal structure that is at least a step nearer reality. A full description of the structures of atoms and crystals involves some of the most difficult questions in modern physics and could not be undertaken in this book. All that is therefore attempted is to provide a picture of metal crystals on which the rest of the subject-matter may be based.

Atoms are minute systems consisting of a nucleus surrounded by electrons each of which carries a charge of negative electricity which is the same for all electrons. Until quite recently the nucleus was supposed to consist of electrons and positively charged protons, but it has now been found that atomic nuclei also contain other components. For the present purpose, however, it is sufficient to consider the nucleus of an atom as composed of electrons and protons, the electrical charge on a proton being equal and opposite to that of an electron. All atomic nuclei contain more protons than electrons and consequently are positively charged, and the magnitude of this positive charge determines the number of electrons that surround the nucleus. Thus, if the nucleus of a particular atom contains five more protons than electrons, the atom will contain five electrons surrounding the nucleus. The mass of the atom is concentrated in the nucleus which is extremely small compared with the space occupied by the whole system. The dimensions of nuclei are of the order of 10^{-12} cm. diam. while those of atoms are of the order of 10^{-8} cm. diam.

Originally it was assumed that the electrons occupied fixed positions around the nucleus, then they were supposed to travel in certain orbits, but it is now agreed that the positions or movements of the electrons cannot be pictured and all that can be said is that they form an atmosphere round the nucleus. In this atmosphere the density of distribution of electrons varies with the distance from the nucleus, but although it becomes low towards the outer limits of the sphere of influence of the atom, it does not vary in a regular manner with the distance from the nucleus.

Classification of the Elements.

There are 92 different kinds of atoms distinguished from each other by the excess of protons over electrons in the nucleus and the number

of electrons surrounding the nucleus. These correspond to the 92 elements, and, when the elements are arranged in the order of their atomic weights, the ordinal number of an element in this series (i.e. its atomic number: Table 11) gives the number of electrons surrounding the nucleus of its atom. Thus the number of electrons varies from 1 in the atom of hydrogen to 92 in that of uranium. Beginning with the hydrogen atom more complex structures are built up in stages, the end of each stage being reached when a stable configuration of electrons is obtained. The end of the first stage is reached at helium with 2 electrons, the end of the second stage at neon with $2+8$ electrons, the end of the third stage at argon with $2+8+8$ electrons, the end of the fourth stage at krypton with $2+8+8+18$ electrons, the end of the fifth stage at xenon with $2+8+8+18+18$ electrons, and the end of the sixth stage at niton with $2+8+8+18+18+32$ electrons.

TABLE 11

<i>Elements</i>		<i>Electrons</i>	<i>Atomic no.</i>
Hydrogen	H	1	1
Helium	He	2	2
Lithium	Li	2+1	3
Beryllium	Be	2+2	4
Boron	B	2+3	5
Carbon	C	2+4	6
Nitrogen	N	2+5	7
Oxygen	O	2+6	8
Fluorine	F	2+7	9
Neon	Ne	2+8	10
Sodium	Na	2+8+1	11
Magnesium	Mg	2+8+2	12
Aluminium	Al	2+8+3	13
Silicon	Si	2+8+4	14
Phosphorus	P	2+8+5	15
Sulphur	S	2+8+6	16
Chlorine	Cl	2+8+7	17
Argon	A	2+8+8	18
Potassium	K	2+8+8+1	19
Calcium	Ca	2+8+8+2	20
Scandium	Sc	2+8+8+1+2	21
Titanium	Ti	2+8+8+2+2	22
Vanadium	V	2+8+8+3+2	23
Chromium	Cr	2+8+8+5+1	24
Manganese	Mn	2+8+8+5+2	25
Iron	Fe	2+8+8+6+2	26
Cobalt	Co	2+8+8+7+2	27
Nickel	Ni	2+8+8+8+2	28
Copper	Cu	2+8+8+10+1	29
Zinc	Zn	2+8+8+10+2	30
Gallium	Ga	2+8+8+10+3	31
Germanium	Ge	2+8+8+10+4	32
Arsenic	As	2+8+8+10+5	33
Selenium	Se	2+8+8+10+6	34
Bromine	Br	2+8+8+10+7	35
Krypton	Kr	2+8+8+10+8	36

OF PURE METALS

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TABLE 11—continued

<i>Elements</i>		<i>Electrons</i>	<i>Atomic no.</i>
Rubidium	Rb	2+8+8+18——+1	37
Strontium	Sr	2+8+8+18——+2	38
Yttrium	Yt	2+8+8+18+ 1+2	39
Zirconium	Zr	2+8+8+18+ 2+2	40
Niobium	Nb	2+8+8+18+ 4+1	41
Molybdenum	Mo	2+8+8+18+ 5+1	42
Masurium	Ma	2+8+8+18+ 6+1	43
Ruthenium	Ru	2+8+8+18+ 7+1	44
Rhodium	Rh	2+8+8+18+ 8+1	45
Palladium	Pd	2+8+8+18+10——	46
Silver	Ag	2+8+8+18+10+1	47
Cadmium	Cd	2+8+8+18+10+2	48
Indium	In	2+8+8+18+10+3	49
Tin	Sn	2+8+8+18+10+4	50
Antimony	Sb	2+8+8+18+10+5	51
Tellurium	Te	2+8+8+18+10+6	52
Iodine	I	2+8+8+18+10+7	53
Xenon	Xe	2+8+8+18+10+8	54
Caesium	Cs	2+8+8+18+18 — —+1	55
Barium	Ba	2+8+8+18+18 — —+2	56
Lanthanum	La	2+8+8+18+18+ —+1+2	57
Cerium	Ce	2+8+8+18+18+ 1+1+2	58
Praseodymium	Pr	2+8+8+18+18+ 2+1+2	59
Neodymium	Nd	2+8+8+18+18+ 3+1+2	60
Ilminium	Il	2+8+8+18+18+ 4+1+2	61
Samarium	Sm	2+8+8+18+18+ 5+1+2	62
Europium	Eu	2+8+8+18+18+ 6+1+2	63
Gadolinium	Gd	2+8+8+18+18+ 7+1+2	64
Terbium	Tb	2+8+8+18+18+ 8+1+2	65
Dysprosium	Ds	2+8+8+18+18+ 9+1+2	66
Holmium	Ho	2+8+8+18+18+10+1+2	67
Erbium	Er	2+8+8+18+18+11+1+2	68
Thulium	Tm	2+8+8+18+18+12+1+2	69
Ytterbium	Yb	2+8+8+18+18+13+1+2	70
Lutecium	Lu	2+8+8+18+32+ 1+2	71
Hafnium	Hf	2+8+8+18+32+ 2+2	72
Tantalum	Ta	2+8+8+18+32+ 3+2	73
Tungsten	W	2+8+8+18+32+ 4+2	74
Rhenium	Re	2+8+8+18+32+ 5+2	75
Osmium	Os	2+8+8+18+32+ 6+2	76
Iridium	Ir	2+8+8+18+32+ 7+2	77
Platinum	Pt	2+8+8+18+32+ 8+2	78
Gold	Au	2+8+8+18+32+10+1	79
Mercury	Hg	2+8+8+18+32+10+2	80
Thallium	Tl	2+8+8+18+32+10+3	81
Lead	Pb	2+8+8+18+32+10+4	82
Bismuth	Bi	2+8+8+18+32+10+5	83
Polonium	Po	2+8+8+18+32+10+6	84
..	..	2+8+8+18+32+10+7	85
Niton	Nt	2+8+8+18+32+10+8	86
Radium	Ra	2+8+8+18+32+18——+1	87
Actinium	Ac	2+8+8+18+32+18——+2	88
Thorium	Tn	2+8+8+18+32+18+1+2	89
Protactinium	Pa	2+8+8+18+32+18+3+1	90
Uranium	U	2+8+8+18+32+18+4+1	91
		2+8+8+18+32+18+5+1	92

The elements helium, neon, argon, krypton, xenon, and niton with stable configurations of electrons in their structure are the inert gases. Their atoms do not combine with other atoms to form compounds nor do they readily combine amongst themselves to form crystals. Other elements form compounds and crystals because their atomic structure is not stable and they tend to achieve stability by detaching, attaching, or sharing electrons. The kind of crystals and compounds formed by these other elements depend on whether they detach, attach, or share electrons and on the number of electrons available for these purposes.

In Table 11 the elements are arranged in the order of their atomic weights. The first column contains the name of the element and the second its symbol. The third column shows the numbers of electrons in the different groups, while the fourth gives the atomic number. The lines drawn across the table indicate the completion of a stable arrangement of atoms at the elements helium, neon, argon, &c.

Table 11 does not indicate exactly how the shells of electrons are built up in actual atoms, but, while not strictly in accordance with atomic structure, it shows how the classification of the elements into different periods is arrived at on the basis of it. The first period consists of hydrogen and helium, a stable configuration of two electrons being realized in the latter. At lithium a second shell of electrons begins to form and electrons are added one by one to this shell until a stable arrangement is reached at neon. Then at sodium a third shell begins to form and is completed at argon. After that the building-up process becomes more complicated. It is the number of electrons in the last column that principally determines the behaviour of an atom in combination with other atoms, and these are known as the valency electrons. Potassium and calcium develop normally from argon by the addition of one and two valency electrons respectively. At scandium, however, a group of electrons that are not valency electrons begins to form, and this continues to copper in which this group is complete with ten electrons. Copper has the same number of valency electrons as potassium, and zinc has the same number as calcium. From copper to krypton the development is the same as from lithium to neon and from sodium to argon, i.e. by the progressive addition of one valency electron. At krypton a stable arrangement of electrons is again reached. Rubidium and strontium develop normally from krypton. Then at yttrium another group begins to form and continues to palladium. Normal development begins again at silver which has the same number of valency electrons as rubidium, and this continues to the completion of another stable configuration at xenon. Caesium and barium develop from xenon by the addition of one and two valency electrons, but at lanthanum two other groups begin to form. One of these is complete at lutecium and the other at gold. Then from gold to niton normal development proceeds with the addition of valency electrons one at a

time. Finally No. 87 and radium develop normally from niton and in actinium the building up of another group begins.

If the four series of elements in which groups of electrons other than valency electrons are being formed are omitted a very simple relationship between the remaining elements is disclosed as shown in Table 12 in which hydrogen and helium are not included.

TABLE 12

Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca	Ga	Ge	As	Se	Br	Kr
Rb	Sr	In	Sn	Sb	Te	I	Xe
Cs	Ba	Tl	Pb	Bi	Po	85	Nt
87	Ra						

From lithium to neon the number of valency electrons increases from 1 to 8, and the same progressive change takes place between sodium and argon. At potassium the building up of a new group of valency electrons on the stable configuration of argon begins. Potassium is related to sodium by having one valency electron and calcium is related to magnesium by having two. Then comes the series of elements scandium to nickel which are not included in Table 12, and at copper the formation of a group of valency electrons begins again. Copper is related to sodium by having one valency electron and zinc is related to magnesium by having two. From gallium to krypton the number of valency electrons increases from three to eight as in the series aluminium to argon. In the next period the same conditions are realized. First come rubidium and strontium related to sodium and magnesium respectively, then the series yttrium to palladium not included in Table 12, and finally the normal series silver to xenon. In the next period, caesium to niton, the conditions are again repeated when the series lanthanum to platinum is left out.

A much simpler version of Table 12 could be obtained by leaving out potassium, rubidium, and caesium, and calcium, strontium, and barium. Then the elements remaining would fall into eight groups represented by the vertical rows. These groups are numbered from left to right, and to distinguish the series potassium, rubidium, and caesium from copper, silver, and gold, the former are included in a sub-group (*a*) and the latter in a sub-group (*b*). Calcium, strontium, and barium are distinguished from zinc, cadmium, and mercury in the same way, and owing to the fact that copper, zinc, gallium, germanium, &c., silver, cadmium, indium, tin, &c., and gold, mercury, thallium, lead, &c.,

combinations the atoms attain greater stability by detaching, attaching, or sharing electrons. If the three transition series, scandium to nickel, yttrium to palladium, and lanthanum to platinum, are excluded, the atoms of the elements helium to radium consist of a nucleus, a stable configuration of electrons corresponding to that of the preceding inert gas, and a certain number of additional electrons. It is these additional electrons that take part in combinations. They are known as the valency electrons and the last figure in the table of electrons in Table 11 gives the number of these in the structure of the various elements. The nucleus and the electrons in the stable arrangement corresponding to that of the preceding inert gas may in the meantime be termed the core of atoms.

All the inert gases except helium contain eight electrons in the outer or valency group. All the other elements contain less than this number, and they tend to form combinations in which they can complete the group of eight by attaching or obtaining a share in other electrons or in which they can detach the electrons outside the stable core. In many of the elements the arrangement of the electrons in the stable core is the same as in the preceding inert gas, but this does not apply in all cases. Following the elements through Table 11 it is seen that in the series lithium to fluorine the valency group is superimposed on an arrangement of electrons similar to that in helium, in the series sodium to chlorine it is superimposed on an arrangement similar to that in neon, and in potassium and calcium on an arrangement similar to that in argon. From scandium to nickel the process of forming the valency group remains in abeyance while another group is formed. When the total number of electrons in these two groups reaches ten the series of elements copper to krypton begins to develop on the basis of the argon configuration $+10$. In rubidium and strontium the valency group is superimposed on the krypton structure, then from yttrium to palladium the process of forming the valency group again remains in abeyance while another group is formed. When the total number of electrons in these two groups reaches 10, the series silver to xenon develops on the basis of the krypton structure $+10$. In caesium and barium the valency group is based on the xenon structure, then at lanthanum two groups and at cerium three groups begin to form. This transition is completed at platinum when the total number of electrons in the three groups is 24. From gold to No. 85 the series develops on the basis of the xenon structure $+24$. Thus, in addition to the stable configurations characteristic of the inert gases, there are three other comparatively stable arrangements on which valency groups are based, viz. the argon structure $+10$, the krypton structure $+10$, and the xenon structure $+24$.

In all the elements except the transition elements the valency group is superimposed on a stable or comparatively stable arrangement. The atoms of these elements therefore enter into combinations in which they can complete the valency group or detach the electrons in it. In

the transition elements, however, there are other incomplete besides the valency groups, and as the electrons may move from one group to another, the number of electrons that the transition elements contribute to combinations is variable.

In considering the combination of atoms attention may be given in the first place to combinations involving the exchange of electrons. If their number of valency electrons is small, atoms tend to detach electrons so as to leave a stable configuration corresponding to that of the preceding inert gas (or one of the provisionally stable arrangements). Thus the atoms of lithium, sodium, potassium, &c., tend to detach one electron, and those of calcium, strontium, and barium two electrons. If their number of valency electrons is large, atoms tend to attach electrons so as to attain a stable configuration corresponding to that of the next inert gas (i.e. with 8 electrons in the valency group). Thus fluorine, chlorine, bromine, and iodine tend to attach one electron and attain the arrangements of electrons characteristic of neon, argon, krypton, and xenon respectively. It is obvious that in combinations of this kind two different sorts of atoms must be involved, so that the atoms that tend to attach electrons will obtain them from atoms that tend to detach them. Furthermore, the two sorts of atoms must combine in such proportions that the number of detached electrons equals the number of attached electrons. Thus lithium, sodium, potassium, rubidium, and caesium combine with fluorine, chlorine, bromine, and iodine in equal atomic proportions, while calcium, strontium, and barium combine with fluorine, chlorine, &c., in the proportions of one atom of one of the elements of the former group to two atoms of one of the elements of the latter group. Examples of the resulting combinations are NaCl, KCl, KI, NaBr, and CaF₂, BaCl₂, &c.

The atom of an element is electrically neutral because the positive charge on the nucleus is balanced by the sum of the negative charges on the electrons. When an atom enters into combination and attaches or detaches electrons, it is no longer neutral, for while the nucleus remains unaltered the number of electrons is changed. The remainder of the atom carries a charge and is known as an ion. If the atom has detached electrons it is a positive ion, and if it has attached electrons it is a negative ion. Ions are represented by symbols like Na⁺, Fe⁺⁺, and Cl⁻ in which the dots indicate the number of unit positive charges acquired by detaching electrons and the dashes indicate the number of unit negative charges acquired by attaching electrons.

Combinations involving the sharing of electrons may next be considered. A good example of this type is provided by carbon in the form of diamond. Carbon has four valency electrons, and in diamond each carbon atom shares its four electrons with each of four neighbours. Each carbon atom has then a share in eight electrons, i.e. its own four and one from each of its four neighbours, and this constitutes a stable arrangement. Many other combinations are formed in the same way:

thus hydrogen atoms combine in pairs so that the two electrons are shared by both atoms; in silicon each atom shares its four electrons with four neighbours as in diamond; in silicon carbide the two kinds of atoms combine in the same way as do the carbon atoms in diamond and the silicon atoms in silicon; and in numerous other compounds such as calcium carbide (CaC_2), carbon tetrachloride (CCl_4), gaseous chlorine, bromine, and iodine (Cl_2 , Br_2 , I_2), sulphur dioxide (SO_2), and organic crystals, the same conditions prevail.

In addition to the above types of combination between atoms which involve the exchange or sharing of electrons there exists another force of attraction known as the van der Waals force. This is responsible for the crystallization of the inert gases at sufficiently low temperatures, and the molecules of many organic compounds, each of which has a complete and self-sufficient internal system of valency bonds, are held together by this relatively weak force.

Crystals.

When atoms combine by exchanging electrons, the resulting combination is known as ionic or heteropolar. When they combine by sharing electrons the resulting combination is known as co-valent or homopolar. There are two general types of crystals corresponding to these two types of combination. In ionic crystals the lattice points are occupied by ions, and these are maintained in position with respect to each other by electrostatic attraction between ions of different sign. In homopolar crystals the lattice points are occupied by atoms, and these are maintained in position with respect to each other by sharing electrons.

Sodium chloride is a typical ionic crystal and its space-lattice is shown in Fig. 24 in which the black circles represent sodium ions and the white circles represent chlorine ions. Taken together the two kinds of ions form a simple cubic lattice, while each kind forms a face-centred cubic lattice. The black and white points are therefore equivalent. In the crystal each sodium atom has become a positive ion by detaching an electron and each chlorine atom has become a negative ion by attaching an electron. The bonding of the ions in the crystal depends on the electrostatic attraction between them.

Diamond is a typical homopolar crystal. Its space-lattice, shown in Fig. 9, consists of two interpenetrating face-centred lattices represented respectively by black and white circles. Each of the atoms represented by a white circle is surrounded by four of those represented by black circles, and the arrangement is such that these four black circles are situated at the corners of a tetrahedron. The atom represented by the white circle shares one of its four valency electrons with each of the four atoms represented by black circles. If the diagram in Fig. 9 was

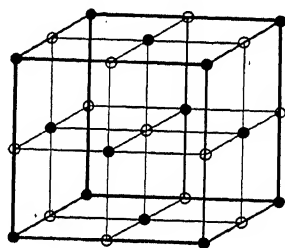


FIG. 24. Space-lattice of sodium chloride.

further extended, it would be seen that each of the black atoms is similarly surrounded by four white atoms situated at the corners of a tetrahedron. Each black atom also shares one of its four valency electrons with each of four neighbours.

The formation of crystals of the ionic type requires the presence of two kinds of atoms in definite atomic proportions. Crystals of the homopolar type may be formed by two or more kinds of atoms or by atoms of one kind only, as in diamond, silicon, or solid nitrogen. When homopolar crystals are formed from atoms of two or more kinds, the atoms must be present in definite atomic proportions so that all valency electrons will be shared. For the construction of a homopolar crystal out of identical atoms it is necessary for each atom to be able to complete its outer group of eight electrons by sharing electrons with each of the requisite number of neighbours. If the atom contains four valency electrons, it forms homopolar crystals by sharing those with four neighbours. If it contains five, six, or seven valency electrons it can complete its outer electron shell by sharing three, two, or one electrons with the equivalent number of neighbouring atoms. If, however, it contains less than four valency electrons, it cannot complete a stable group of eight by sharing these. It is therefore necessary for the valency electrons to be so disposed that each is shared by more than two atoms. This is the way atoms are combined in metallic crystals.

In Table 12 the metals and non-metals are separated by a broken diagonal line, and the line dividing elements with four or more valency electrons from those with three or less lies between carbon, silicon, germanium, tin, and lead on the one hand, and boron, aluminium, gallium, indium, and thallium on the other. As the transition series scandium to nickel lies between calcium and copper, the series yttrium to palladium between strontium and silver, and the series lanthanum to platinum between barium and gold, these transition elements belong to the class of metals with less than four valency electrons. In order to describe the crystal structures of the elements they may be divided into three classes based on Table 13. The first class contains the elements carbon, silicon, germanium, antimony, bismuth, and all to the right of them. These elements form typical homopolar crystals. The second class contains the elements beryllium, magnesium, copper, silver, gold, and all to the left of them. These elements form typical metallic crystals. The third class contains the remaining elements boron, aluminium, zinc, gallium, cadmium, indium, tin, mercury, thallium, and lead in which intermediate conditions are realized.

The characteristic feature of homopolar crystals is that the number of immediate neighbours of each atom is equal to eight minus the number of valency electrons in the structure of that atom. Thus, if the valency is n , each atom in homopolar crystals has $8-n$ close neighbours. Of the elements in the first class described above, carbon, silicon, and germanium have four valency electrons, and each of those elements crystal-

lizes with the tetrahedral cubic (i.e. diamond) structure described above in which each atom has four neighbours. Arsenic, antimony, and bismuth have five valency electrons and they form crystals of the rhombohedral hexagonal type in which each atom has three close neighbours, i.e., each atom shares one electron with each of three neighbours. Selenium and tellurium have six valency electrons, and in the crystals of these elements the atoms are arranged in spiral chains so that each atom has two neighbours. Finally, in crystals of iodine which has seven valency electrons the atoms are arranged so that each has one close neighbour. In this class therefore all the solid elements form crystals in which the $8-n$ rule is obeyed.

The second class consists entirely of metals, i.e. beryllium, magnesium, copper, silver, gold, and all to the left of them in Table 13. All these elements have one or two valency electrons, and all except manganese form crystals with body-centred cubic, face-centred cubic, or close-packed hexagonal lattices. In these lattices each atom has respectively eight, twelve, and twelve equidistant neighbours. It is evident that when the number of valency electrons is less than four, the $8-n$ rule cannot be obeyed, and in the class of elements under consideration atoms with one or two valency electrons form crystals in which each has eight or twelve neighbours. These crystals are not built up on the basis of each atom sharing a certain number of electrons with the same number of neighbours. Instead, the valency electrons are detached and form a lattice of electrons, and the crystals may be described as an assemblage of ions and free electrons. This is the typical metallic type of crystal. The number of neighbours and the directions in which they are situated is not determined by the electronic structure of the atoms, and the crystals are built up on the basis of close packing. In crystals of this type atoms of different kinds behave in a similar way, and this has a pronounced effect on the combinations formed between metallic atoms of different kinds as described in Chapter V. The electrical conductivity of metals depends on the fact that their crystals contain free electrons which are available for carrying current.

It remains to consider the elements of the third class. Of these, zinc, cadmium, and mercury have two valency electrons, aluminium, gallium, indium, and thallium three valency electrons, and tin and lead four valency electrons. These elements may be divided into three groups: (a) mercury, zinc, cadmium, and gallium in which the $8-n$ rule is to some extent obeyed, (b) aluminium, thallium, lead, and indium in which the structure closely resembles that of typical metallic crystals, and (c) tin in which one form (α -tin) is homopolar and another (β -tin) resembles the elements in group (b). Mercury (two valency electrons) crystallizes with a simple rhombohedral structure (i.e. a distorted simple cubic structure) in which each atom has six close neighbours. The $8-n$ rule is therefore obeyed. Zinc and cadmium crystallize with the close-packed hexagonal structure, but the lattice is modified so that

each atom has six instead of twelve close neighbours and the $8-n$ rule is again obeyed. Thus in the close-packed hexagonal cell, obtained by packing spheres as shown in Fig. 6, the ratio of the length of the vertical (c) axis to that of the horizontal (a) axis is 1.633 : 1. In such an arrangement each atom has twelve close neighbours. In zinc and cadmium, however, the axial ratio is approximately 1.9 and this means that the horizontal planes of atoms (Fig. 6) are farther apart than in the normal structure. Consequently, each atom has six neighbours in the same horizontal plane which are closer to it than the two sets of three neighbours in the planes above and below. Although the $8-n$ rule is obeyed in mercury, zinc, and cadmium in so far as the number of neighbours is concerned, it is evident that the other typical condition of homopolar crystals, i.e. that each atom completes an outer shell of eight electrons by sharing one electron with each of the requisite number of neighbours, cannot be fulfilled. These elements have two valency electrons and in the crystals each atom has six neighbours. Thus the crystals resemble homopolar crystals with respect to the number of neighbours and metallic crystals with respect to the method of sharing electrons. When the crystal structure of gallium was first determined, it was thought to obey the $8-n$ rule, but later work showed that the structure was more complicated, and although it may be described as a distorted form of structure with five close neighbours the deformation destroys this characteristic.

Aluminium, β -thallium and lead crystallize in the face-centred cubic form, α -thallium crystallizes in the close-packed hexagonal form, and although the crystal structure of indium is actually tetragonal, the difference in length of the (a) and (c) axes is so slight that the structure may be regarded as a close approximation to the face-centred cubic. Thus these elements form typical metallic crystals, but they differ from the main group of metals to the left of copper, silver, and gold in Table 13 in that the atoms are not completely ionized, i.e. all the valency electrons are not detached from the atoms and included in the electron lattice. Finally, tin with four valency electrons crystallizes in the tetrahedral cubic (diamond) lattice in the α form and thus forms typical homopolar crystals, while in the β form it crystallizes in a tetragonal lattice in which the atoms are incompletely ionized. It should be added in conclusion that this section is based on the writings of Hume-Rothery (10) which should be consulted for fuller information.

Combination in the Gaseous and Liquid States.

Attention has so far been almost exclusively confined to combinations between atoms in the solid state. In order to complete this section combination in the gaseous and liquid states may be considered briefly.

A gas may consist of atoms, molecules, or ions. Thus, when a metal is vaporized, the constituent particles of the resulting gas are the atoms of the metal concerned. Similar conditions prevail in the inert gases.

Most well-known gases consist, however, of molecules. Thus the constituent particles in hydrogen are molecules consisting of two atoms united by a homopolar bond. The same applies to nitrogen, oxygen, fluorine, chlorine, bromine, sulphur dioxide, carbon dioxide, and steam. When X-rays are passed through a gas, it is ionized to an extent that is related to the intensity of the X-ray beam. It then consists of electrons and residual ions.

When an element is melted, the constituent particles of the resulting liquid may be atoms or molecules united by the homopolar bond. When a compound is melted the constituent particles of the liquid may either be atoms, molecules, or ions. Most molten compounds consist of molecules, but some decompose into their constituent atoms on melting and others are ionized. Molten salts such as sodium chloride, potassium chloride, and calcium fluoride, are partially ionized, and because current can be carried through the liquid by the migration of ions these compounds are known as non-aqueous electrolytes.

When a compound is dissolved in some other substance, it can retain its identity by breaking up into molecules or ions. If it breaks up into molecules, it retains its identity because each molecule contains the atoms in the same proportions as in the solid compound. If it is ionized, it retains its identity because ions are parts of a compound. Thus, when sodium chloride is dissolved in water, it consists partly of sodium and chlorine ions and partly of sodium chloride molecules. Even if it were completely ionized, it would still be sodium chloride, for a solution of sodium and chlorine would contain atoms of these elements and not ions.

METAL SURFACES

We have dealt so far with the structure of metal crystals and with the conditions that prevail at the boundaries between the individual crystals in an aggregate. It remains to consider the boundaries between crystals and their external environment, i.e. metal surfaces. Discussion of this will not be confined, however, to a description of the conditions that prevail at metal surfaces, for whereas the behaviour and properties of crystals and crystal boundaries are dealt with in succeeding chapters, only some aspects of the behaviour of metal surfaces are dealt with in other parts of the book, and consequently it is necessary to discuss some of their properties here.

If we consider the atoms in the interior of a crystal, we see that each atom is surrounded by a certain number of neighbours disposed in a certain way and that the capacity of the atoms for combining is completely satisfied. This condition does not exist, however, at the exposed surface of a crystal, for the outermost atoms have no neighbours on one side. From this, two consequences will be seen to arise. In the first place, the positions taken up by the atoms in the outermost layer relative to those in the next layer will be different from what they

would be if the atoms in the outermost layer were subjected to the normal symmetrical attractions. Secondly, the capacity for combining of the atoms in the outermost layer will not be completely satisfied. The atoms in the outermost layer are thus chemically unsaturated and are said to possess residual affinity which enables them to combine readily with anything that has access to the surface. It is this property with which we are concerned. There is clearly some similarity between the conditions that exist at the boundary between two crystals and those that prevail at the exposed surface of a crystal. In both cases the lattice is distorted, but the nature and degree of distortion differs, and whereas atoms on a surface are known to possess residual affinity, it is not known whether atoms at a boundary are also chemically unsaturated. If they are, it will be to a much smaller extent than at the surface, and as the information about crystal boundaries is scanty, the analogy cannot be developed.

No surfaces are molecularly smooth, i.e. owing to the existence of minute pits and elevations the number of atoms actually exposed at the surface is greater than would be calculated by taking account of the geometrical surface area and the packing of the atoms. This gives rise to the conception of specific surface which is obtained by multiplying the area of the geometrical surface by a factor. The value of the factor varies with the condition of the surface. It is a minimum for a polished surface and is increased by abrading, etching, or subjecting the surface to alternate oxidation and reduction. Thus, for a geometrical surface of unit area Bowden and Rideal found the following values for the specific surface of nickel sheet treated in different ways: rolled 3.5, rolled and annealed 7.7, sandpapered 9.7, activated by oxidation and reduction 46.

If a metal surface is obtained by condensation from vapour in a high vacuum, it is in a substantially virgin condition, but immediately it is exposed to the atmosphere the residual affinities of the surface atoms cause a layer of gas to become attached to the surface, i.e. adsorbed. Depending on the temperature, pressure, nature of the metal and of the gas to which it is exposed this adsorbed layer may develop into a surface film of oxide or some other compound, and from the adsorbed layer or surface film gas atoms may diffuse into the metal and behave there in a variety of ways. Various features of this group of phenomena are discussed in other parts of the book, e.g. the formation and growth of oxide and other films on different metals under different conditions of temperature, pressure, and atmosphere is dealt with in Chapter VIII, the diffusion of gases in metals is considered in Chapter VI, and the effects of this diffusion are described in a number of sections. In the meantime, attention may be confined to adsorption and to the relations between it and film formation and diffusion. This section will then be concluded with an account of the effects of polishing and related treatments.

In discussing the combination of atoms it was pointed out that in addition to the combining forces arising from the exchange or sharing of valency electrons, there is another type of attraction known as the van der Waals force, which is responsible for the crystallization of the inert gases at sufficiently low temperatures and the bonding of the molecules of certain organic compounds. This force also gives rise to a type of adsorption known as physical adsorption in which a single layer of gas molecules is held on the metal surface by the van der Waals force. One of the characteristics of physical adsorption is that it is not specific, i.e. all gases, including the inert gases are adsorbed in this way by all metals. Another characteristic is that the amount of gas adsorbed at a given temperature increases with the pressure. A third characteristic is that the amount of physical adsorption that occurs under a given pressure decreases as the temperature increases, and although it is considerable at a temperature of -180°C. , it is practically negligible above atmospheric temperature. Furthermore, physical adsorption takes place very rapidly, i.e. equilibrium between the gas and the metal surface is attained in a short time and the amount of adsorption changes rapidly with changes in temperature and pressure.

The type of adsorption that is most important from the point of view of this work is that known as activated adsorption or chemisorption. In this case the gas atoms or molecules are held on the surface of the metal by the residual affinities of the surface layer of metal atoms. This type of adsorption becomes effective at temperatures at which physical adsorption is negligible. It increases with temperature up to a maximum and then begins to decrease. Thus, if adsorption under constant pressure is plotted against temperature, say for the case of carbon-monoxide and palladium, it is found to decrease as the temperature is raised from -200°C. to -80°C. (physical adsorption), then to increase with temperature up to 0°C. , and finally to decrease again (activated adsorption). With this type of adsorption equilibrium is reached slowly and the surface condition does not alter rapidly with changes in temperature and pressure.

When a virgin metal surface is exposed to a gas, some of the gas molecules which strike the surface are immediately held there by the unsaturated surface atoms. Some of the molecules later evaporate and others condense, so that the amount of gas adsorbed under particular conditions depends on the balance between condensation and evaporation. In general, the maximum adsorption that can be attained is a layer of gas one molecule thick. The residual affinities of the surface atoms are then satisfied and a condition of kinetic equilibrium exists between the layer of adsorbed gas and the surrounding atmosphere. The pressures at which this condition is realized are of the order of one atmosphere. At lower pressures only a fraction of the metal surface is covered by gas molecules.

Two features of activated adsorption are important from the point

of view of subsequent chapters. As this phenomenon depends on the surface atoms of the metal combining with the gas, there must be some affinity between the metal and the gas, and thus, in contrast with physical adsorption, activated adsorption is specific, i.e. certain metals adsorb certain gases. The inert gases, for example, are not adsorbed in this way by any metals, nitrogen is not adsorbed by copper, and hydrogen does not appear to be adsorbed by gold or silver. As a further consequence of the combination between the metal atoms and the gas, the gas molecules tend to be dissociated, and thus it is atoms rather than molecules that are adsorbed. It is this that accounts for the promotion of inter-gas reactions in the presence of metal surfaces and for the use of metals as catalysts. Furthermore, as gases diffuse into metals in the atomic condition, the conversion of molecules into atoms by adsorption is the first stage in the process, and the only gases that diffuse into metals are those that are adsorbed, i.e. diffusion is also specific.

Although activated adsorption involves combination between the gas and metal atoms, it differs from the formation of a compound in that only the residual affinities of the metal atoms are involved. For the formation of a true compound the conditions relating to the gas, metal, temperature, and pressure must be such that the gas atoms have a greater affinity for the metal atoms than these latter have for each other. Then the metal atoms are detached from their combination with each other and caused to combine with the gas atoms. This phenomenon is not restricted to the outermost layer of metal atoms, and consequently, when the conditions are such that a compound may form, the adsorbed layer quickly becomes a film of oxide or other compound which increases in thickness as rapidly as the gas can diffuse through the already existing film to the underlying metal. The growth of oxide films is fully described in Chapter VIII, and for a more complete account of adsorption reference should be made to *Gases and Metals* by C. J. Smithells (11). Meanwhile, it will be enough to say that gases may diffuse into metals either from adsorbed layers or surface films and that this diffusion is an important phenomenon in the treatment of metals.

In phenomena such as oxidation and corrosion it is the surface rather than the body of the metal that is involved, and it is also at the surface that wear, grinding, abrasion, sliding friction, and polishing have their effects. In many practical applications the ability of metals to resist wear is important and a considerable amount of attention has recently been given to its study. This work has shown that wear in general is a very complicated phenomenon, and that the wear-resistance of a metal under a given set of conditions can only be determined by tests conducted under these or closely related conditions. Grinding and polishing are important in the preparation of certain classes of metal products for service, and they have also been the subject of a

considerable amount of scientific study. The purpose of the present section is to describe as briefly as possible the changes produced in metal surfaces by the above processes and to establish some sort of relations between them. It will be shown that at least four effects are produced by the above-mentioned processes, and that in general the processes differ in the relative magnitude of these effects. The four effects concerned are: (1) true abrasion, which involves cutting the metal surface and the removal of particles of metal, (2) deformation, which involves a change in the crystal structure of the remaining surface, (3) chemical action, which involves reactions between the surface and the atmosphere to which it is exposed, and (4) heating, which serves to increase the other effects and frequently results in actual melting at the surface.

Rubbing a metal surface with emery paper is a typical example of abrasion. The most evident feature of this operation is that grooves are cut in the metal surface and particles of metal are removed in the form of powder. As the fineness of the emery increases, the grooves become smaller, and by using papers of increasing fineness and gradually replacing coarser by finer grooves the surface may be progressively improved. This removal of particles of material is true abrasion, but rubbing with emery produces other effects. One of these is deformation or flow. The changes produced in metals by deformation are considered in the next chapter where it is shown that when a metal is caused to flow, the crystal structure is distorted and the metal hardened. The tearing away of metal particles during abrasion, and the rubbing of the abrasive over the surface, cause deformation of the metal that remains. Distortion and hardening occur and the metal is said to be worked. When coarse emery is used, this working effect penetrates the metal to a considerable extent, which varies, of course, with the hardness of the metal, and the effect of the deformation can easily be observed microscopically. As the fineness of the emery is increased, the depth of penetration of the working effect diminishes, but it does not necessarily follow that the more localized effect produced is less severe. One of the objects of rubbing metals on progressively finer papers when preparing them for microscopic examination is to remove the worked layer produced by coarse papers by means of finer papers which have less penetrating effects, and ultimately to obtain such a shallow worked layer that it is removed by etching.

Removal of metal particles (true abrasion) and distortion and hardening of the remaining surface (working) are two of the components of the processes under consideration. A third is chemical action. All the metals except the noble metals, i.e. silver, gold, platinum, rhodium, osmium, and iridium, are capable of reacting with the atmosphere at ordinary temperature and forming oxide films on the surface. Once the first film is formed oxygen must diffuse through it to reach the underlying metal, and therefore the rate at which the film increases in

thickness becomes progressively less as oxidation proceeds. At atmospheric temperature the rate of oxidation falls almost to zero while the film is extremely thin, and the common metals are said to be protected from oxidation by this film. The processes under consideration remove this film, but in so far as they involve abrasion they also cause a certain amount of disintegration of the remaining surface which becomes much more active because of the irregularities and crevices produced, i.e. the specific surface area is increased. Furthermore, these processes heat the surface and in this way promote oxidation, and the net result is that oxidation is an important component in wear, abrasion, &c. Electrochemical corrosion (Chapter VIII) differs from oxidation in that it only occurs in the presence of moisture, but when it does occur it is also a component of wear, &c., for the abrasion produces new surfaces for corrosion which in turn assists in removing each successive surface presented. In the case of iron and steel it appears that atmospheric nitrogen may also be absorbed during wear, and as this tends to embrittle the steel it accelerates the removal of material.

It is well known that the friction involved in the processes under consideration causes the generation of heat, but definite information on the high surface temperatures reached has only recently become available from the work of Bowden and Ridler (12). These investigators found in the first place that when two metals were rubbed together, high temperatures, which varied with the load, speed, coefficient of friction, and thermal conductivity of the metals, were reached. In the case of fusible metals such as gallium, Wood's metal, bismuth, and lead, the temperature at the sliding surface soon reached the melting point of the metal and could not be further raised by increasing the load or speed of rubbing. With metals of high melting-point, temperatures as high as $1,000^{\circ}\text{C.}$ were reached at the surface. In later experiments it was shown that when metals were rubbed on a given substance, the loss of weight due to abrasion depended on the melting-point rather than the hardness of the metal. Thus when lead (melting-point 327°C. and Vickers Hardness 5.0) and gallium (melting-point 30°C. and Vickers Hardness 6.6) were rubbed on filter paper under the same conditions with respect to load and speed, the low-melting gallium lost weight about ninety times as rapidly as the lead. Finally, it was shown that the efficiency of a polisher depends on its melting-point in relation to that of the metal. Thus camphor (m.p. 178°C.) could be used to polish Wood's metal (m.p. 68°C.) but had no influence on tin, lead, or zinc. Oxamide (m.p. 417°C.) readily polished these metals, but had no effect on copper, while lead oxide (m.p. 888°C.) polished all metals of lower melting-point but not nickel and molybdenum which, however, could be polished with high-melting oxides such as chromic oxide, &c. These results indicate that in the operation of polishing high temperatures tend to be attained at the surfaces of contact, and in general the melting-point of the polishing powder or the metal surface will be reached. If

the melting-point of the polishing powder is lower than that of the metal it will be ineffective, and for efficient polishing the melting-point of the powder must be higher than that of the metal so that the surface of the latter may be melted. It is not essential that the surface of the metal should reach its melting-point in order that it may be polished. The strength of metals decreases rapidly with rising temperature and becomes very low near their melting-point, and it is therefore possible to produce the surface flow required without melting. In such cases, however, polishing is slow, and in typical polishing operations it appears that the surface of the metal reaches its melting-point.

Confirmation of the above experiments is provided by numerous observations that have been made on steel wires, locomotive tyres, rails, &c., that have been subjected to friction. It is well known that steel may be hardened by rapid cooling from a high temperature and in this condition it exhibits a characteristic microstructure known as the martensitic structure (Chapter XI). If steel does not have this structure when put into service, it can only be produced by heating the metal to about 800° C. and cooling rapidly. It has frequently been observed that a thin layer with the martensitic structure can be formed on steel components subjected to friction, and this indicates that this layer must have been heated to about 800° C. by the friction and cooled rapidly by the flow of heat from the surface into the remainder of the metal. As this layer is of appreciable depth—about 0.03 in.—its presence indicates that much higher temperatures were reached at the outermost surface.

In the processes variously known as wear, grinding, abrasion, sliding friction, and polishing, the four components, removal of material, deformation of the surface, chemical action, and heating are involved. In so far as the processes can be distinguished from each other the distinction is due to a different combination of these components, and in different examples of the same process the various components have different degrees of importance. Each of the components is a complicated phenomenon when considered in detail, and when the relations between them have to be taken into account, the subject becomes very difficult. The characteristic feature of true abrasion is that particles of metal are removed from the surface, and although rubbing with emery papers of increasing fineness may be said in a general sense to polish a surface, in scientific metallurgy this term is applied to a different process. Thus, in the final polishing of metal specimens on selvyt, chamoisleather, or broadcloth, moistened and impregnated with a finely powdered oxide, it is not the abrasive action of the powder that is important, but the fact that the surface is deformed and the ridges worked down to fill the hollows. If we distinguish true abrasion and polishing in this way we may say that all the processes under consideration combine these two components in different ways, and that the rise in temperature which occurs facilitates both abrasion and polishing,

while chemical action facilitates the former and has an uncertain effect on the latter. In abrasion and grinding, the removal of material is the most important factor; in polishing, surface deformation is most important; in sliding friction both are important in varying degrees which depend on load, speed, condition of surfaces, and metals concerned, while wear is a general term used to cover all sorts of processes in which either abrasion or polishing may predominate. Whichever factor is predominant in a given case, it must be remembered, however, that all the others are also involved to a greater or lesser extent.

We have already seen that in the process of abrasion the ridges that remain and the underlying surface are deformed, i.e. the crystal structure is distorted and the metal hardened. Furthermore, in sliding friction between dry surfaces and in wear generally some deformation occurs. The mechanism of deformation and the changes that accompany it are considered in the next chapter, but it is necessary to include here some account of the changes produced at a metal surface during polishing. As already explained, the characteristic feature of polishing is that a considerable amount of localized flow takes place and from the ridges left by fine abrasives is worked down into the hollows. This is a particular case of deformation or flow in that a thin layer of metal is intensely affected and is probably melted, and the nature of the surface produced has been the subject of considerable scientific attention. In a series of papers from 1903 onwards Beilby described his experiments on polishing which led him to the conclusion that the essential feature of the polishing process was to cause the surface layer to flow like a liquid then to solidify rapidly without crystallization, thus forming an amorphous or vitreous surface layer. His work was collected and published in a book in 1921 (13). The hypothesis of the 'Beilby Layer' was extensively debated by metallurgists, some of whom accepted the idea that this layer was amorphous, while others contended that it consisted of minute crystal fragments. In the absence of evidence the controversy died out after a time, but the development by Davisson, and Germer of the electron diffraction method of determining the structure of surfaces, and the application of this to the investigation of polished surfaces has reopened the discussion in the last few years. The work that has been done in the study of polished surfaces between 1933 and 1936 is reviewed by Finch (14) and it is only necessary to say here that this work confirms Beilby's hypothesis, i.e. polished surfaces have been shown to consist of a close-packed assembly of atoms which has no relation to the normal crystal structure of the metal and resembles the arrangement of atoms characteristic of liquids. This conclusion is in conformity with the recent work on the temperatures reached during polishing, and it appears that in this process the surface layer of metal is melted and caused to solidify rapidly in a substantially structureless, i.e. amorphous or vitreous condition. The original controversy is not definitely concluded, however, for an amorphous layer is not clearly

distinguished from one consisting of extremely minute crystals containing a few atoms and oriented at random. Most of those who have studied the subject agree, however, that the 'Beilby Layer' may be described as amorphous, and it may be added that in specimens polished by the usual metallurgical methods the thickness of the layer is about 30 Ångstrom units. Below this, small crystals appear and increase in size until the normal crystalline structure of the metal is found substantially unaltered.

CHAPTER III

DEFORMATION AND FRACTURE

THE most important characteristics of metals are those involved in their response to applied force, i.e. their mechanical properties. In practically every application of metals they are expected to withstand some kind of forces without deforming or breaking; in the mechanical shaping operations employed in preparing them for service they are expected to deform without breaking, and in the tests that are employed for determining the suitability of metals for various purposes the response to applied force is again involved. The mechanical behaviour of metals in service, shaping operations, and tests, depends on certain fundamental relations between the characteristics of metals on the one hand and applied force on the other, and the purpose of the present chapter is to describe the way in which metals respond to force, ignoring for the time being the effects of time and temperature, which are dealt with in Chapter IV, and of repeated application of force, which are dealt with in Chapter VII. Before beginning the detailed consideration of the fundamental aspects of the response of metals to force, it is advisable, however, to give a brief outline of some features of this, and to say something about the relations between mechanical properties on the one hand, and service, fabrication, and testing on the other.

Consideration may be given in the first place to the type of forces that may be applied and the conditions under which they may operate. Many different types of force may be applied. They may tend to stretch, compress, bend, shear or twist, or do several of these things at the same time. Starting from zero the applied force may be gradually increased, a constant load may be applied for a long time, or the metal may be subjected to a sudden shock. Progressively increasing or suddenly applied forces that fail to break a metal in one application may be applied repeatedly, and any of the conditions mentioned above may be applied to a metal at any temperature below its freezing point. Thus, in general, in considering the forces applied, the following factors have to be taken into account:

Nature of force. Tension. Compression. Bending. Torsion. Shear

Temperature of Application

Conditions of Application

<i>Progressively increased</i>	<i>Suddenly applied</i>	
Magnitude	Magnitude	Magnitude
Number of applications	Number of applications	Time of
Rate of increase	Rate of application	

In general, applied force first produces deformation and then fracture. This is not universally true, for very hard metals may fracture under certain conditions without undergoing an appreciable amount of deformation, and very soft metals under certain conditions (e.g. under compressive forces) may deform continuously without fracturing. In order to explain clearly the response of metals to applied force, deformation and fracture must be considered separately, and it is the relations between force and deformation, force and fracture, and deformation and fracture that constitute the phenomena on which the mechanical properties of metals depend.

When force is applied to metal two kinds of deformation may be produced, viz. elastic, and permanent deformation. The amount of elastic deformation increases with the applied force and disappears when the force producing it is removed. The amount of permanent deformation also increases with the applied force, but under certain conditions it may continue under a constant force or even under a decreasing one. When the force producing it is removed, the permanent deformation remains. These two different kinds of deformation involve different kinds of changes in the metal crystals. Usually both kinds take place at the same time, but under certain conditions either may take place alone. In considering mechanical properties the relations between force and elastic deformation, between force and permanent deformation, and between elastic and permanent deformation are important. Thus, in general, in dealing with the response of metals to applied force the relations between the force and fracture, elastic deformation, and permanent deformation respectively, as well as the mutual relations between these phenomena, have to be taken into account.

Most of the practical applications of metals depend primarily on their mechanical properties. In use they are required to withstand various kinds of forces applied under many different conditions without undergoing any appreciable amount of deformation and without breaking. The shaping of metals in preparation for use also depends to a great extent on their mechanical properties, and in such operations as extrusion, forging, hot- and cold-rolling, hot-stamping, cold-pressing, and cold-drawing they are required to deform readily without breaking. The forces applied in service and during fabrication are usually very complex, and in order to ascertain whether a given metal is more suitable than another for a particular purpose it is generally necessary to make the experiment itself. Some preliminary indication of suitability may, however, be obtained by testing. The tests used fall into two categories. In the first may be placed those in which the conditions of service, or of a particular fabricating operation, are imitated as closely as possible while still satisfying the requirements of a standardized and reproducible test. In the second may be placed those that are used to study the behaviour of metals under specified conditions that are not necessarily related to those which obtain either in service or fabrication. Tests of

this second type are the more widely used of the two. They neither imitate the conditions of use nor determine the fundamental mechanical properties, but the behaviour of metals in these tests ultimately depends on the same fundamental attributes as their behaviour in service. Thus the results of the tests are indirectly related to behaviour in service, and from long experience in their use their significance is now fairly well understood. It is not possible to infer from any test exactly how a metal will behave either in use or fabrication, but some indication of its suitability can always be obtained. When dealing with similar metals their relative suitabilities can generally be ascertained, but the chief use of

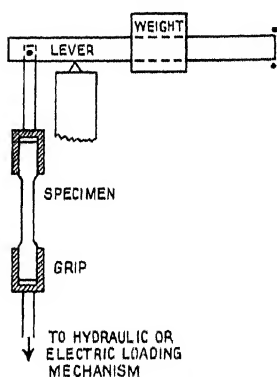


FIG. 25. Diagram of tensile test.

tests is for the purposes of specification and inspection. When experience has shown that a given metal is suitable for a particular purpose, the properties required may be specified on the basis of test results. Then each batch of metal may be subjected to tests in order to discover whether it satisfies the specification, i.e. has similar properties to the metal previously used successfully.

Apart from their use in connexion with the determination of the suitability of metals for different applications, the standardized tests are extensively employed in investigating the phenomena that are the ultimate basis of mechanical properties. It is these phenomena with which this chapter is concerned, and in terms of the behaviour of metals in the test, this will now be described.

THE TENSILE

In this test a specimen of metal is subjected to the action of a progressively increasing tensile pull until it breaks. The machine used is shown diagrammatically in Fig. 25. It consists essentially of two parts—a means of applying a force and a means of measuring it. The part exerting the force is attached to one end of the specimen and the part measuring it to the other. The force is usually applied by a hydraulic cylinder or by a geared electric motor, while the measuring apparatus consists of a lever arm supported on a knife-edge. The shackle holding one end of the specimen is attached to the lever arm on one side of the knife-edge, and the force applied to the specimen is balanced by moving a jockey weight along the other side of the arm. Tensile test specimens are usually either round or flat bars. They may be made with screwed ends to hold in screwed grips, or with plane ends which are gripped by means of toothed wedges. To prevent the specimen breaking in the grips the ends have a larger cross-sectional area than the portion

between. This has parallel sides and is connected to the larger ends by means of a fillet of large radius. Fig. 26 shows two test-pieces as used in the tensile test, viz. a round bar with screwed ends and a flat bar with plane ends.

In considering the properties of metals as illustrated by their behaviour in this test, one important characteristic of the test must be kept in mind. The arm of the lever that carries the jockey weight rests on a stop. The load indicated by the position of the weight on the lever is not applied to the specimen until the end of the lever is raised off the stop. Thus the load indicated by the position of the weight is the force transmitted through the specimen from the hydraulic cylinder to the

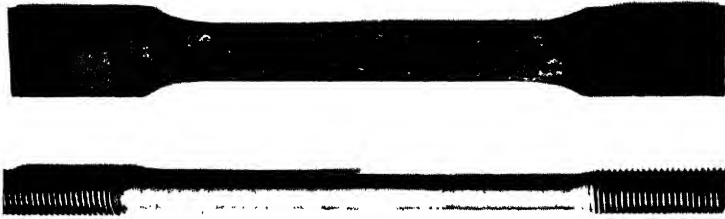


FIG. 26. Tensile test-pieces.

lever arm. If a specimen is subjected to a load under which it deforms continuously, it stretches without lifting the lever arm. If, however, the lever arm is kept above the stop while the load is increased or decreased it means that at any instant the specimen transmits without deformation the load indicated by the weight. In other words this load is a measure of the resistance of the specimen to deformation. If a rod of plasticine is placed in a tensile-testing machine it stretches without transmitting any appreciable load. The lever carrying the jockey weight is therefore not lifted. If a rod of quartz is used it undergoes very little deformation and transmits a progressively increasing load until it breaks. The characteristic feature of metals in general is that they deform appreciably as the load is increased and stop deforming when the load is kept constant. Thus, their behaviour is intermediate between that of plasticine and quartz, and although stretching is taking place, the jockey weight is balanced until a certain maximum load is applied.

When the specimen is fixed in the machine and the tensile pull gradually increased, the metal stretches and the extension between two gauge marks is measured as the test proceeds. When the extension is small, a special instrument known as an extensometer is used to measure it. When it is large, it can be measured by means of dividers. It is

usual in tensile tests to measure the applied load and the extension produced.

The effect of a given load depends on the cross sectional area of the test-bar. The extension produced by a given load depends on the length of bar over which it is measured. To eliminate the effect of cross-sectional area and gauge length the applied load is divided by the cross-sectional area of the test piece, giving what is termed the *stress*; and the extension between the gauge marks is divided by the gauge length, giving what is termed the *strain*. The stress is stated in tons or pounds per sq. in. or kg. per sq. mm. The strain is stated in inches per inch. A tensile test is carried out by increasing the load in steps and measuring the extension at each step. When the test is concluded a curve must

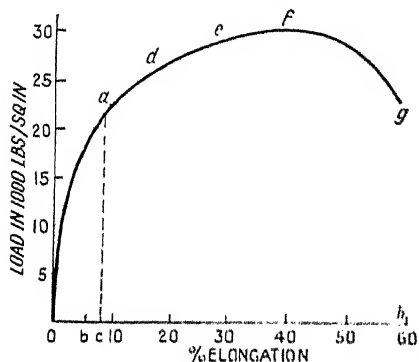


FIG. 27. Load-extension curves of copper.

be plotted to illustrate the behaviour of the metal. In this it is usual to plot the applied load divided by the original cross-sectional area against the total extension divided by the original gauge length. This is sometimes called a stress strain curve, but it is also called a load extension curve in which the load is expressed in tons per sq. in. and the extension as a percentage of the original gauge length.

Load-Extension Curves.

A typical load extension curve obtained in a tensile test is shown in Fig. 27. The metal concerned is copper, and in the curve the load in tons per sq. in. of the original cross-sectional area is plotted against the elongation expressed as a percentage of the original length. During the test permanent and elastic deformation take place simultaneously, and the method of separating them will be described presently. Meanwhile, attention may be devoted to the characteristics of the curve shown.

As the load is increased from zero to the value represented by the point *f*, the metal extends under an increasing load. Thereafter it extends under a decreasing load and finally breaks at *g*. In order to determine accurately the part of the curve between *f* and *g* the jockey weight must be moved along the lever arm so as to keep the arm above the stop shown in Fig. 25. If the lever rests on the stop, the load carried by the specimen is not shown, and all that can be said is that it is less than that indicated by the position of the jockey weight.

Up to the point *f* the metal extends under an increasing load. If the load is kept constant at any intermediate point, say at *a*, *d*, or *e*, no further appreciable deformation occurs in the case of iron, nickel,

copper, aluminium, and their alloys at atmospheric temperature. But this statement does not hold for lead, tin, zinc, and their alloys at atmospheric temperature or the other metals at elevated temperatures. It follows from this that when, in the case of copper, the load has been increased from zero to a and the metal extended by the amount oc , the test-bar is more resistant to deformation than at the beginning. This resistance increases as deformation proceeds. The load a can extend the test-bar by the amount oc , but in order to obtain further extension it must be increased. In dealing with metals the term hardness is used to mean resistance to deformation, and it is evident from the form of the curve in Fig. 27 that when copper is deformed its hardness is increased.

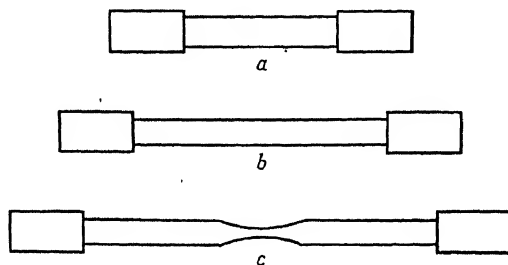


FIG. 28. Illustrating uniform and local extension.

This is known as hardening by deformation. It is one of the most important characteristics of metals. Among the common ones it is displayed in a pronounced degree by iron, nickel, copper, aluminium, and their alloys, but it is much less marked in lead, zinc, tin, and their alloys.

While the metal is extending under an increasing load, the extension is uniform over the length of the test-bar. When, however, extension under a decreasing load begins at f it becomes localized, and at a certain point in the bar a neck is formed. The three drawings in Fig. 28 may be taken to represent (a) the original bar, (b) the bar after uniform extension under an increasing load, and (c) the bar after localized extension under a decreasing load. Fracture eventually takes place at the smallest cross-section in the neck.

True Stress-Strain Curves.

Tensile tests are usually conducted in the manner described above, and the behaviour of the metal under test is represented by a curve in which the stress, obtained by dividing the load by the original cross-sectional area, is plotted against the strain, obtained by dividing the extension by the original gauge length. Such curves are of the same shape as those obtained by plotting the load against the extension, and the only result of converting these to stress and strain respectively is that the results obtained with specimens of different cross-sectional area or different gauge length become comparable. In order to understand

the significance of the behaviour of a metal in the tensile test it is necessary, however, to consider certain other types of curves that may be obtained.

At the beginning of the test the applied load divided by the original cross-sectional area gives the true stress, but as the specimen stretches, its cross-sectional area diminishes and the true stress, i.e. the stress per unit of actual area, is actually greater than that obtained by the above method. If, however, the change in diameter during the test is measured, the true stress at each stage can be calculated. While the extension is uniform, the diameter may be measured at any point on the parallel portion, but when necking begins it must be measured at the smallest cross-section. When the first small increment of extension is divided by the original gauge length, the result may be accepted as a measure of the strain applied to the metal. Obviously, however, the next increment of extension is produced on a length greater than the original gauge length, and to obtain the true strain, the extension should be divided not by the original gauge length but by the length from which it was produced. In general, as extension proceeds, the distance between the gauge marks increases, and each successive increment of extension is produced on a greater length than the preceding increment. To obtain the true strain each increment of extension should be referred to the length from which it was produced instead of the original gauge length, and a method of doing this has been proposed by Ludwik (588). By this method the true strain may be obtained for the portion of the test in which the extension is uniform, but when the neck begins to form, the strain is not uniformly distributed over the gauge length. During this stage in the test no further strain is produced in the portion outside the necked region, and in this region the strain varies gradually and reaches a maximum at the bottom of the neck. It is the strain at this point that is important, but serious experimental difficulties are involved in measuring the change in length over a very short length.

As the extension of a specimen during the tensile test is accompanied by a decrease in its diameter, the change in diameter, or some quantity calculated from it, may be used in a measure of the strain. When this is done, the measurements may be made at the smallest diameter and the effect of unequal distribution of strain may thus be eliminated. Curves of several types have been drawn in which the true stress, obtained by dividing the applied load by the actual cross-sectional area, is plotted against some quantity derived from measurement of the change in diameter. Stead (589) plotted the true stress against the percentage reduction of diameter and obtained curves of the type represented by curve *A* (Fig. 29). This curve shows that the true stress increases progressively throughout the test until the metal fractures at *c*, and a characteristic feature is that the curve is linear between *d* and *c*. Several workers have plotted the true stress against the percentage reduction in area and obtained curves similar to *A*

(Fig. 29) except for the fact that the portion between d and c is concave upwards. Both these types of curves are subject to the criticism that the reduction in diameter or area is always referred to the original diameter or area in the same way as extension measurements are usually referred to the original gauge length. MacGregor (590) has,

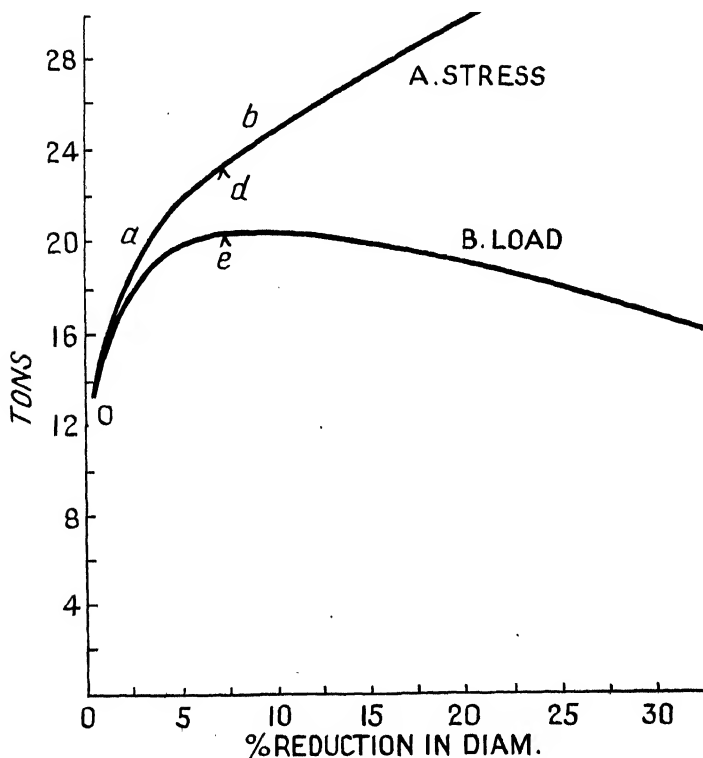


FIG. 29. *A* stress and *B* load against reduction in diameter.

however, devised a method of obtaining curves in which each increment of reduction in area is referred to the area from which it is produced. These curves are of the same form as *A* (Fig. 29), and the portion between d and c is linear. For the present purpose attention may be confined to the curves obtained by Stead by plotting the true stress against the reduction in diameter, and these may be compared with curves obtained by plotting the stress (or load) against the reduction in diameter and with the usual type of stress-strain or load-extension curve as shown in Fig. 27.

Two curves obtained by measuring the change in diameter are shown in Fig. 29. The metal concerned is steel, which undergoes elastic deformation only in the early stages of the test and for this reason the curves begin at *o* instead of at the point of intersection of the axes. The percentage reduction in diameter is used as a measure of the amount of deformation taking place. In curve *B* the applied load divided by the original cross sectional area is plotted against the percentage reduction in diameter. In curve *A* the applied load divided by the actual cross-sectional area at each stage in the test is plotted against the percentage reduction in diameter. The curves relate to a specimen having an original cross-sectional area of 1 sq. in. At the beginning of the test, i.e. before any appreciable amount of deformation has taken place, the two curves coincide, i.e. the original and the reduced cross-sectional areas are approximately the same. As deformation proceeds, however, the cross-sectional area decreases and the load curve falls below the true stress curve.

The conditions in a tensile test are such that the applied load is balanced by the resistance of the specimen to deformation, and in curve *A* (Fig. 29) the applied load is divided by the actual cross sectional area at each stage. Thus, any point in curve *A* indicates the resistance of unit area of the metal to deformation at that particular stage in the test. Taken as a whole this curve shows the increase with deformation of the resistance to deformation per unit of cross sectional area. From the first application of the load until fracture occurs at *e* the resistance to deformation per unit of area increases. In the early stages (*o* to *a*) a small amount of deformation produces a large increase in resistance, i.e. resistance to deformation increases rapidly. Later (*a* to *d*) this increases more slowly, and it finally assumes an approximately constant value between *d* and *e*.

Curve *B* represents the change in the resistance to deformation of the test-bar as a whole. This is equal to the resistance to deformation per unit of area multiplied by the cross-sectional area. As the test proceeds, the resistance to deformation per unit of cross-sectional area increases as shown by curve *A*. At the same time the cross-sectional area decreases. In the first stage of the test the increase in the resistance to deformation per unit of area is more rapid than the decrease in cross-sectional area. The product, resistance to deformation per unit of area multiplied by the cross-sectional area, increases as shown by the portion *oe* of curve *B*. But in the later stage of the test the increase in the resistance to deformation per unit of area is less rapid than the decrease in cross-sectional area. The product therefore decreases as shown by the part *ef* of curve *B*.

Curve *B* (Fig. 29) resembles the curve in Fig. 27 in that in both cases the load is divided by the original cross-sectional area, and both curves show that the resistance to deformation of the test-bar as a whole increases to a maximum and then decreases. Point *e* in Fig. 29 has the

same significance as point *f* in Fig. 27. These represent the greatest load (in tons or pounds per sq. in. of the original cross-section) that the metal sustains in the course of a tensile test. This is called the ultimate or maximum tensile stress or strength.

Curve *A* (Fig. 29) is of fundamental significance and represents the rate at which the metal hardens when deformed by a tensile pull. In this curve the resistance to deformation per unit of cross-sectional area is plotted against the percentage reduction in diameter, but it may equally well be plotted against any other quantity obtained by measuring the smallest diameter. Other features of the behaviour of metals in a tensile test may be deduced from this curve. Between *o* and *d* the slope is changing progressively, and the rate of increase in the resistance to deformation per unit of area is more than enough to compensate for the decrease in the cross-sectional area. Beyond *d* the rate of increase in the resistance to deformation per unit of area is not enough to compensate for this. Thus the maximum tensile strength represented by point *e* on curve *B* corresponds to the point on curve *A* at which the slope becomes less than a certain minimum.

Uniform and Localized Extension.

Up to the point *f* (Fig. 27) the test-bar extends uniformly. Beyond it the extension is localized. The beginning of necking coincides with the maximum tensile strength, i.e. when the resistance to deformation of the whole cross-section of the test-bar begins to decrease the deformation is restricted to a short length of the specimen. The explanation of this coincidence is as follows:

A round tensile test-bar may be supposed to consist of a large number of very thin discs of metal. To obtain uniform extension over a given length of the parallel portion each of the discs included in this length must extend equally. If the stress was the same in each disc and if they were all composed of identical material, there is no reason why the extension should not be uniform. Neither of these conditions is satisfied, however, in this test. The load is applied through grips that act on the surface at the ends of the test-piece. The stress near the ends is therefore not a tensile stress distributed uniformly over the cross-section. As the distance from the ends increases, the stress in the bar does approximate more closely to a tensile stress acting uniformly over the whole cross-section. This is the type of stress that is most effective in producing deformation, and other things being equal, the reduction in diameter will tend to increase with the distance from the grips, and to reach a maximum in the middle of the specimen. But in addition to this, even a pure metal consisting entirely of crystals of the same kind is not absolutely uniform from the point of view of resistance to deformation, for, as will be shown presently, the deformation of a metal crystal is closely related to its orientation with respect to the direction of stress. Accordingly, in each of the supposed discs there will be numerous

crystals of different orientations. In some of them the orientations of certain crystals or groups of crystals will be such as to offer a greater resistance to deformation than the crystals in other discs. Therefore, the test-bar may be considered to be divided up into discs which vary in their resistance to deformation, and this, combined with the unequal distribution of stress, will tend to cause some portions to deform more readily than others.

The uniform extension of metal test pieces subjected to tension is due to their ability to harden by deformation. It may be supposed that when the load is first applied some portions of the specimen deform more readily than others. As a result of this, however, their resistance to deformation is increased. Thus, by deformation, the discs that were originally most susceptible to it are hardened until their resistance becomes equal to that of the others. When the load is increased, these in their turn deform and are also hardened. Thus, although deformation always tends to take place where there is least resistance, it causes an increase of this resistance at the points where it takes place. Consequently, so long as the resistance to deformation increases with deformation, the extension will be uniform over the length of the test-piece. This condition is realized up to the point of maximum tensile strength. Beyond this, further deformation is accompanied by a decrease in the resistance to deformation of the cross section. Thus, whenever one particular portion is deformed more than the remainder, subsequent deformation is confined to this and a neck is formed.

General Consideration of Deformation in Tension.

The type of curve shown in Fig. 27 is that usually determined in a tensile test. It does not have the same direct fundamental significance as curve *A* (Fig. 29), but it is more easily determined, has long been familiar, and is of course closely related to it. The shape of the curve between *o* and *f* depends on the rate at which resistance to deformation increases. If a small amount of deformation produces a large increase in resistance to it, the curve is steep, whereas if a large amount of deformation is required to produce a small increase in resistance to it, the curve is flat. Its form depends on the portion *od* of curve *A* (Fig. 29). So long as the slope of this does not become less than a certain minimum it may vary considerably in shape, and these variations are reflected in curves of the type shown in Fig. 27. The form of the portion *od* of curve *A* (Fig. 29) determines the amount of uniform extension and the maximum tensile strength. These quantities may therefore be said to depend on the rate at which the metal hardens under deformation and the extent to which this proceeds. If a metal hardens rapidly under deformation, it will have a high maximum tensile strength. If it hardens more slowly, it will have a high uniform elongation. If, however, it hardens slowly, and this continues for some time without the rate of hardening falling below the minimum required for uniform extension,

then the maximum tensile strength and the uniform extension will both be high.

The portion *fg* of the curve in Fig. 27 depends on the slope of the portion *dc* of curve *A* (Fig. 29), and on the position of the point *c* on this latter curve. *c* indicates the stress per unit of cross-sectional area required to produce fracture, i.e. the breaking stress. If the breaking stress was less than that indicated by *c*, fracture would occur after a smaller amount of reduction in diameter, and the local extension, on which the portion *fg* of Fig. 27 depends, would be less. If, however, the breaking stress was greater than that indicated by *c*, fracture would occur after a greater amount of reduction in diameter and the local extension would be greater.

It is worth while at this stage to consider the significance of the breaking stress and its relations to other aspects of the behaviour of metals in a tensile test. Iron differs from most other metals in that it has a definite resistance to permanent deformation, i.e. as the stress is increased from zero only elastic deformation occurs until a certain stress is reached. This is considered later. Most of the other metals whose mechanical properties have been studied do not exhibit this initial resistance to permanent deformation. Thus copper, aluminium, gold, silver, lead, tin, and zinc, and many other metals, begin to undergo permanent deformation as soon as stress is applied. As the initial resistance to permanent deformation may be said to be zero (or practically so), the shape of the stress-strain curve must depend entirely on the rate at which resistance to deformation increases as deformation proceeds. This increase in resistance to deformation is due to certain changes produced in the crystal structure of the metal by the deformation, as described later. During a tensile test the resistance to deformation per unit of actual area increases progressively (curve *A*, Fig. 29), and finally a point is reached at which the resistance to deformation is greater than the resistance to fracture. Instead of deforming further the metal then breaks, and we may therefore say that metals fracture in tension when the resistance to deformation has been increased to a point at which it exceeds the resistance to fracture. Many non-metallic substances, e.g. quartz, fracture in a tensile test without previously undergoing permanent deformation. Manganese, arsenic, antimony, and bismuth, which have crystal structures differing from those of other metals, also fracture without much previous deformation, and the same applies to a number of alloys. Results obtained in tensile tests of materials that fracture without previous deformation are, however, unreliable, and it is difficult to say that the specimens have actually been broken by a tensile pull. In any case, the characteristic feature of metals is that they do not fracture until they have undergone a certain amount of permanent deformation. As we cannot break the metal without first deforming it, we have no way of discovering its inherent resistance to fracture. We can say that it fractures when the resistance

to deformation has been increased to a point at which it exceeds the resistance to fracture, or when the deformation has produced a certain amount of change in the crystal structure. We can study these changes in the crystal structure, but even when these are fully understood it is difficult to discover whether they exert their effect by increasing resistance to deformation or by diminishing resistance to fracture.

The different elementary metals exhibit different behaviour in the tensile test. Great alterations in the behaviour of most of these metals may be produced by alloying them with other elements in different amounts and combinations. Furthermore, the behaviour of any metal or alloy may be modified by subjecting it to deformation before testing, and that of many alloys may be modified by thermal treatment. Consequently, when metals and alloys are considered generally, a great variety of different behaviours in the tensile test is possible. Ultimately, however, all these differences may be shown to depend on a comparatively small number of factors which are combined in different ways. One metal may differ from another in its initial resistance to deformation, and that with the lowest initial resistance will begin to undergo permanent strain at a lower stress than the other. This, however, only affects the early portion of the stress-strain curve. Thereafter the behaviour depends in the first place on the rate at which the resistance to deformation increases, i.e. on the rate of what is known as strain-hardening. If this is rapid the stress-strain curve will be steep, if it is slow the curve will rise more slowly. Secondly, it depends on the extent to which the rate of strain-hardening remains higher than is required to counterbalance the reduction in area. This affects the ultimate tensile stress and the uniform elongation. Finally, it depends on the breaking stress, and on the amount of deformation required to strain-harden the metal to such an extent that the resistance to deformation exceeds the resistance to fracture. This affects the reduction in area at the point of fracture and the local extension. Thus if the breaking stress is the same, the metal that strain-hardens most slowly will give the largest reduction in area at the point of fracture, because more deformation will be required to make the resistance to deformation greater than the resistance to fracture. If, however, the rate of strain-hardening is the same, the metal with the highest breaking stress will give the greatest reduction in area at the point of fracture.

It is evident from the foregoing that the maximum tensile strength will be high when a metal hardens rapidly under deformation or when this hardening proceeds at a rate exceeding a certain amount for an appreciable time. The uniform elongation will be high when a considerable amount of deformation takes place before the rate of hardening falls below the minimum necessary to counterbalance the reduction in cross-sectional area. The local elongation will be high when the metal does not harden appreciably under deformation and draws down to a small cross-section before fracture. It will be shown later that a metal with a

very high resistance to deformation may break under a small stress in a tensile test on account of its small resistance to fracture under the conditions of the test. Disregarding this, however, it may be said that the highest maximum tensile strength should be obtained from a metal that hardens rapidly under deformation. In this case the high maximum tensile strength will be accompanied by a small total extension. Then as the rate of hardening under deformation decreases, the maximum tensile strength will decrease, accompanied first by an increase in uniform extension, and then by a decrease in uniform extension and an increase in local extension. There is a certain relationship between the maximum tensile strength and the uniform extension, because both depend on the same part of curve *A* (Fig. 29). But the local extension depends on different factors and it tends to be high when the maximum tensile strength and uniform extension are low.

Measurements made in the Tensile Test.

Complete load-extension curves like that shown in Fig. 27 are not as a rule determined in a tensile test. It is usually considered sufficient to measure the maximum tensile strength, the total elongation up to fracture, and the reduction in area at the point of fracture. The strength is stated in tons per sq. in. of the original cross-section, while the elongation and reduction in area are expressed as percentages of the original dimensions. The total elongation includes the uniform and the local extension. The uniform extension is proportional to the gauge length over which it is measured, but the local extension is independent of the gauge length. Furthermore, the uniform extension is greatest when the metal continues to harden under deformation at a rate exceeding a certain minimum, while the local extension is greatest when no appreciable amount of hardening occurs. Thus, when the total elongation is measured and expressed as a percentage of the original gauge length, it includes two quantities that have not the same significance, and one of them is not related to the gauge length at all.

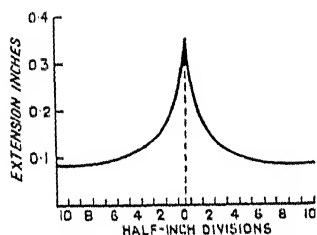
The percentage reduction in area at the point of fracture is independent of the original cross-sectional area, but the extension that takes place in the vicinity of the fracture increases with the cross-sectional area. Thus the local extension is related to the cross-section while the uniform extension is related to the gauge length. If a tensile test-piece is marked off into $\frac{1}{2}$ -in. lengths before testing, and the extension of each length is measured at the end of the test, it is found that it is greatest in the one that includes the fracture, that it decreases on each side of it, and that it finally becomes substantially constant over that part of the bar not affected by the local extension. The result of an experiment of this kind is shown in Fig. 30, which indicates how the total elongation on a length of 10.5 in. is distributed over the $\frac{1}{2}$ -in. lengths into which the specimen is divided. It is clear from this that the total percentage elongation will increase with decrease in the gauge length so long as the

neck is included. It is also clear that when the gauge length is short the total elongation will depend mainly on the local extension, but as it is increased the total elongation will be affected to an increasing extent by the uniform extension.

The uniform extension is proportional to the gauge length and the local extension to the cross-sectional area. The total extension l is therefore given by the formula

$$l = C\sigma a + BL,$$

where C and B are constants, a is the cross sectional area, and L the gauge length. It is evident from this that the relative effects of



a. 30. Distribution of total extension.

local and uniform extension on total extension depend on the relative magnitudes of a and L . In order to obtain comparable values for total elongation with test pieces of different sizes there must be a definite relationship between the cross sectional area and the length over which the total elongation is measured. Different ratios have been recommended in different countries for cylindrical and other shapes of specimens. The recommended ratios

for cylindrical specimens are as follows:

	Gauge length	diameter.
France		
Germany	10	"
Britain	3.54	"

When test-pieces are used which do not conform with these recommended ratios, the length over which the elongation is measured must be stated. Unfortunately, the law of geometrical similarity has not been observed by all those who have determined the tensile properties of different metals, after different treatments, at different temperatures, and with different rates of loading. Consequently, in such cases the results obtained are not comparable.

The foregoing discussion of the relations between gauge length and diameter applies only to specimens in which the material within the gauge length is not affected by the shoulders of the test piece. When the distance between these is less than 2.5 times the diameter of the bar, the maximum tensile strength increases, and the percentage reduction in area decreases as the distance between the shoulders decreases. In general, metals that have a high tensile strength have a low elongation and reduction in area, and when a metal is subjected to a treatment that raises its tensile strength, its elongation and reduction in area are usually decreased. This is due to the fact that the increased rate of strain-hardening, which is the cause of the higher maximum tensile

strength, results in a smaller amount of local extension before the resistance to deformation exceeds the resistance to fracture. This is not universally true, however, and the addition of another element to a pure metal may raise the ultimate tensile stress by increasing the rate of strain-hardening, increase the uniform extension by making the rate of strain-hardening counterbalance the reduction in area for a longer period, and increase the local extension by raising the breaking stress. Thus when zinc, aluminium, and nickel are added to copper, the maximum tensile strength, uniform extension, and local extension and reduction in area may all be increased.

Typical Results of Tensile Tests.

Results of tensile tests on the most widely used metals in the annealed condition are given in Table 14. The values for iron, copper, and aluminium are characteristic of these metals in a condition of very high purity. A figure for nickel of a corresponding degree of purity is not as yet available. Published values relate to metal of less purity and are misleading in comparison with the others. The values for the tensile strength and reduction in area of tin and lead are characteristic of the pure metals, but the elongation found varies greatly with the rate at which the test is carried out as described in Part VI. Owing to their hexagonal crystal structure, zinc and magnesium behave differently from the other metals during deformation, and the results of tensile tests depend to a great extent on their previous treatment. These metals are therefore placed at the bottom instead of in the position corresponding to their tensile strength.

TABLE 14
Tensile Test Results for Pure Metals

<i>Metal</i>	<i>Tensile strength, tons/sq. in.</i>	<i>Elongation % on 2 in.</i>	<i>Reduction in area %</i>
Iron . .	18	45	75
Copper . .	14	58	73
Aluminium . .	4	60	95
Tin . .	1.3	86	100
Lead . .	0.7	118	100
Magnesium . .	11	5	6
Zinc . .	6	66	..

All the metals shown, except magnesium, undergo a substantial amount of deformation before fracture. From iron to lead the tensile strength diminishes while the elongation and reduction in area increase. In lead, tin, and aluminium the total elongation on a 2-in. length is composed mainly of the local extension at the neck, while in copper and iron the uniform elongation that occurs before the commencement of necking contributes more to the result.

Elastic and Permanent Deformation.

Elastic deformation disappears when the force producing it is removed. Permanent deformation remains. Because of this difference it is possible to resolve a curve like that shown in Fig. 27 into two components. If, for example, the load is increased to a (Fig. 31), the extension under load is ob . When the load is removed, the specimen contracts along the line ac . The permanent extension produced by the load a is oc and the elastic extension is cb . Thus the points d and e on the elastic and permanent deformation curves x and y are obtained. When the specimen is again loaded, it extends along ca to a , after which, further permanent deformation begins and extension follows the curve z . At f the total extensi-

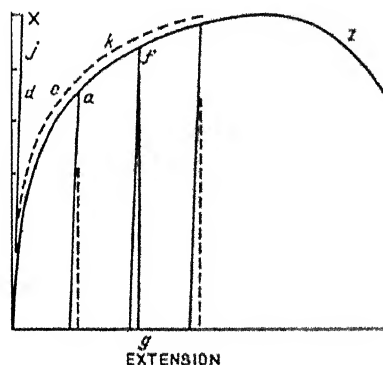


Fig. 31. Elastic and permanent extension.

is og , and if the specimen is unloaded it contracts along the elastic curve to h . Thus the permanent extension produced by the load f is oh and the elastic extension is hg . The points j and k on the elastic and permanent curves are thus obtained. By repeating this procedure at a number of points the complete elastic and permanent deformation curves may be obtained.

According to the above, when the load a is applied and removed the specimen is elastic up to a during subsequent loading. This is not strictly true, however, and when the specimen is again loaded some further permanent deformation occurs. Thus all the permanent deformation that a given load can produce is not produced in the first application. This, and other phenomena associated with repeated loading, will be described more fully in Part III. For the time being it is sufficient to state that after a given load is applied and removed, the metal is approximately elastic within that range, and in order to produce further substantial deformation a greater load must be applied.

Elastic deformation is usually said to be a linear function of the force producing it, and this is known as Hooke's Law. According to Joffé (20), however, this law is only approximately true and its formulation neglected higher order terms in the force function. Deviations from the

straight line law are, however, very small and for most purposes they may be neglected. The slope of the straight line connecting stress and elastic strain is a characteristic attribute of each metal. If F is the tensile load applied to a bar, a the cross-sectional area, L the length over which the extension is measured, and dL the elastic extension, then

$$\frac{F}{a} = f = \text{stress}$$

$$= s = \text{strain}$$

and $\frac{f}{s} = E = \text{Young's modulus of elasticity.}$

Values of this modulus are given in Table 15.

TABLE 15
Young's Modulus of Elasticity

Nickel	30	$\times 10^6$ lb. per sq. in.
Iron	30	$\times 10^6$ „ „
Copper	16	$\times 10^6$ „ „
Aluminium	10	$\times 10^6$ „ „
Tin	6	$\times 10^6$ „ „
Lead	2.6	$\times 10^6$ „ „
Zinc	12.4	$\times 10^6$ „ „
Magnesium	6.25	$\times 10^6$ „ „

As $s = f/E$, s is 1 when $f = E$, i.e. the modulus of elasticity is the stress that would produce an elastic strain equal to the original length, if this were possible. Actually the amount of elastic deformation that can be produced in tension is comparatively small.

The Elastic Limit and the Yield-point.

As elastic deformation is proportional to the applied stress, some will be produced even by the smallest stress. Permanent deformation does not begin, however, until a certain critical stress is applied. Then it begins very slowly and proceeds at an increasing rate as the stress is increased. Up to the stress required to produce permanent deformation the metal is elastic and the load-extension curve is a straight line. This stress is known as the elastic limit or limit of proportionality. The elastic limit is determined by increasing the stress in steps and measuring the strain with a sensitive extensometer. The point at which the stress-strain curve ceases to be a straight line is taken as the elastic limit. As permanent strain begins very slowly the departure from a straight line takes place very gradually, and the stress at which it is first observed depends on the sensitivity of the extensometer. If this has a sensitivity of 0.00001 in. per in., i.e. if it can detect an extension of 0.00001 in. multiplied by the gauge length, then as soon as this amount of permanent

deformation occurs, a departure from linearity will be observed. If, however, its sensitivity is only 0.0001 in. per in. then the departure from linearity must be ten times as great before it is observed. Furthermore, even with the most sensitive extensometers the elastic limit has little significance when the conditions are such that permanent deformation can proceed with time.

Among the common metals iron is unique in that it undergoes no permanent deformation at atmospheric temperature until a considerable stress is applied, namely, from 8 to 10 tons per sq. in. This property is also exhibited by most steels, and their suitability for such a variety of structural purposes depends on the fact that unless the elastic limit stress is exceeded no permanent deformation occurs. This definite limit of proportionality is a property of polycrystalline iron in the range of temperature below about 300° C. In single crystals of iron, and in test-bars containing a few large crystals, the limit of proportionality is much less pronounced. Even in polycrystalline iron the limit of proportionality begins to decrease rapidly at temperatures above 350° C., and as in this range the metal becomes capable of undergoing continuous permanent deformation with time, the limit of proportionality has little significance above 400° C.

The other common metals give load-extension curves of the type shown in Fig. 27. The beginning of permanent deformation is difficult to detect and different estimates of the extent of the elastic range have been recorded. For this reason the elastic or proportional limit is not included in tables of properties. Nickel has a definite elastic limit between 6 and 8 tons per sq. in. in tension, but the elastic limits of copper and aluminium are approximately zero, and the same applies to zinc, tin, and lead, which undergo permanent deformation under constant load at atmospheric temperature.

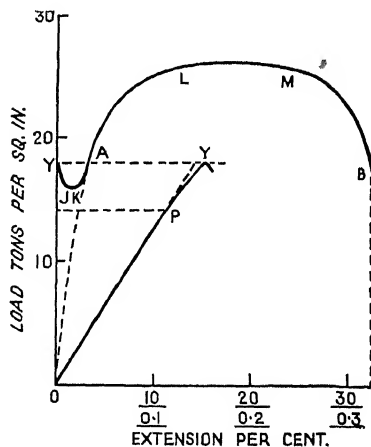
Iron is also distinguished from the other common metals in that at a stress slightly above the limit of proportionality a large amount of permanent deformation takes place suddenly. This is known as the 'Yield-Point', and as deformation beyond the yield-point is on a totally different scale from that below it, the complete load-extension curve of iron cannot be shown on one extension scale. Fig. 32 is a load-extension curve of mild steel in which the deformation before and after the yield-point is plotted on different scales. *OPY* is the curve up to the yield-point, and *OYJKALMB* the full curve on a closer scale. At the point *Y* sudden permanent extension takes place and continues under reduced load as shown by *YJK*. This sudden yielding is a characteristic of polycrystalline iron below 350° C., and in this range of temperature it is exhibited by all alloys in which iron crystals are the predominant constituents. It is, however, not exhibited by single crystals of iron at any temperature nor by polycrystalline iron above 350° C.

In ordinary tensile tests in which the load is measured by running a jockey weight along a beam, the sudden extension at the yield-point

causes the beam to drop on the stop, and all that is observed is that the metal continues to extend under constant load from Y to A and then begins to extend under an increasing load from A to L . By means of machines that give an autographic record of the load required to continue the extension, the curve $YJKA$ may be obtained. The stress at Y is the 'upper yield-point' that at J the 'lower yield-point'. The upper is the one determined in an ordinary tensile test, but the lower seems to be the more fundamental. It is not affected to the same extent by the shape of the cross-section of the specimen nor by the rate of loading. Sometimes the elastic limit is found to coincide with the upper yield-point, sometimes with the lower, and sometimes with neither, and while some investigators have found the decrease in stress between Y and J to be 13-14 per cent., others have found it to be between 27 and 30 per cent. Even approximate agreement cannot be expected between the results of different experiments, for in iron and mild steel the elastic limit and yield-point depend on the average size of the crystals, and several other factors that are not usually taken into account in studying stress-strain curves.

In the other metals the load-extension curve is of the general form represented by $OKALMB$ (Fig. 32), and it is clear that the unique character of the iron curve depends on the fact that the permanent deformation that should take place along OK is inhibited until the stress reaches Y , when all the deformation that should have taken place at lower stresses occurs suddenly. This is the cause of its pronounced yield-point. No other metal exhibits such a point, and it is customary in these cases to define the yield-point as the stress at which a permanent extension of 0.1 per cent. takes place. This is sometimes called the proof-stress to make it plain that it is simply a selected point on a smooth curve, and not in any way equivalent to the yield-point in iron and its alloys. The use of the term proof-stress has not, however, become general, and the yield-points of non-ferrous metals are frequently mentioned.

The above remarks apply to metals in their 'primitive' state, i.e. in such a condition that their properties are not affected by previous deformation. If, however, they are strained before testing, then the previous deformation or working will alter the shape of their stress-strain curve. Thus, if a metal is stressed up to the point a (Fig. 31) and the load removed, the permanent deformation produced by the



32. Load-extension curve of mild steel.

previously applied stress remains. The metal is not elastic up to a during subsequent loading, but the slope of the stress strain curve is much steeper and the limit of proportionality is raised. Thus, while metals like copper, aluminium, silver, and gold, &c., show no limit of proportionality when tested in their primitive state, they have a limit of proportionality after they have been strained. This, however, does not apply to lead, tin, and zinc, for in these metals the effects of deformation are not permanent, i.e. after straining these metals recover their primitive properties in time. In some respects iron behaves in the same way as the other metals. Previous deformation makes the stress strain curve steeper, and the effect of increasing amounts of cold rolling on the curve for mild steel is illustrated in Fig. 271. Once iron has been stressed beyond the yield-point the yield point deformation has been produced and on subsequent loading no yield point is obtained. This is also shown in Fig. 271. The effect of previous straining on the elastic limit is, however, different from that observed with other metals. The high elastic limit characteristic of iron is due to the fact that up to a certain stress permanent deformation is inhibited. Once the metal has been stressed until permanent deformation begins, its capacity for resisting it has been destroyed. Thus although the stress strain curve of previously deformed iron is steeper than that of the metal in its primitive state, it departs from linearity at a lower stress. Thus the elastic properties of iron are said to be impaired by 'overstrain'. The above-mentioned points are further discussed in Chapters IV and VII.

Ductile and Plastic Deformation.

A material that is capable of undergoing an appreciable amount of permanent deformation without breaking, is usually described as plastic. As the metals, iron, nickel, copper, aluminium, lead, zinc, tin, and many of their alloys, are capable of this, they may be described as plastic, and their permanent deformation as plastic deformation. Most plastic materials are capable, however, of undergoing permanent deformation without increase in resistance to deformation, whereas the characteristic property of metals is that under certain conditions permanent deformation is accompanied by an increase in resistance to deformation. To distinguish this from plastic deformation, in which no increase in resistance to deformation occurs, it is known as ductile deformation.

Ductility is the property required in wire-drawing. In this operation metal rod is reduced in diameter by drawing through a tapered hole. For the operation to be successfully accomplished the strength of the reduced section that has passed through the hole must be sufficient to transmit the pull necessary to draw the remainder through. If the amount of reduction in diameter produced in one operation is considerable, the resistance to deformation per unit of area of the reduced section must be greater than that of the unreduced metal. In other words, the metal must be hardened by the deformation performed by drawing

through the hole. The metal must be ductile, and ductility is frequently defined as the capacity to be drawn into wire.

It is, however, difficult to make a sharp distinction between plasticity and ductility. In Fig. 32 it will be seen that when the load is divided by the original cross-sectional area, the resistance to deformation increases rapidly with deformation up to a point between A and L . Then it increases less rapidly to one between L and M , and finally decreases with deformation until fracture takes place at B . From this curve it might be inferred that the metal is ductile up to a point between L and M (i.e. the point of maximum tensile strength), and plastic from this point to fracture. When, however, the load is divided by the cross-sectional area at each stage in the test the curve A (Fig. 29) is obtained, and this shows that the resistance to deformation per unit of reduced area increases progressively until fracture occurs. According to this curve the metal is ductile up to the point of fracture. The question then arises on which curve should the distinction between plasticity and ductility be based.

In all common metals and alloys the resistance to deformation per unit of reduced area increases with deformation up to fracture, as shown in A (Fig. 29). But the rate at which this increases varies considerably. Thus, in lead, tin, zinc, and their alloys, the rate of increase in the resistance to deformation per unit of reduced area becomes less than that required to counterbalance the reduction in area at an early stage in the test. Consequently, the maximum tensile strength is low. In iron and nickel, however, the rate of increase in resistance to deformation per unit of reduced area remains in excess of that required to counterbalance the reduction in area until a considerable amount of deformation has taken place. Consequently, the maximum tensile strength is high. On the basis of curves of the type represented by A (Fig. 29) all metals are ductile up to the point of fracture. On the basis of curves of the type represented by Figs. 27 and 32 they are ductile up to a point and then plastic.

It may now be said that in practice the terms plasticity and ductility are not formally distinguished. It is usual in referring to permanent as distinct from elastic deformation, to speak of plastic deformation, and in referring to the amount of deformation undergone by a metal, to speak of its ductility. Thus plastic is used as a synonym for permanent and ductility is used when the amount of plastic or permanent deformation is under consideration. It is advisable, however, to make some use of the different meanings associated with plasticity and ductility, and this may be done most suitably on the basis of the curves in Figs. 27 and 32. When deformation takes place under an increasing stress (measured on the original cross-section) it is ductile, and when it takes place under a constant or a decreasing load it is plastic. This distinction need only be made, however, when the consequences of the difference are under consideration. When referring to the amount of deformation undergone

by a metal in a tensile test at atmospheric temperature it is more convenient to say that the ductility is high or low, meaning that the total permanent deformation is high or low. This use of the term is justified because ductility is the characteristic property of iron, nickel, copper, aluminium, and their alloys at atmospheric temperature. It is unusual, however, to speak of the ductility of lead or tin for the deformation of these at atmospheric temperature is mainly plastic. The same applies to the deformation of the other metals at elevated temperatures.

Resolved Shear.

Owing to the regular arrangement of the atoms in crystals the mechanical properties of individual crystals are directional, as will be

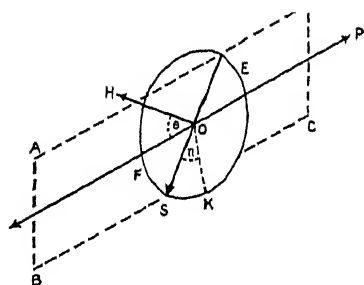


FIG. 33.

described in the next section. A piece of metal composed of many thousands of differently oriented crystals has no directional properties, for those of the individual crystals cancel out in the aggregate. Thus a test-bar of polycrystalline metal may be regarded as an isotropic substance, i.e. with no directional properties.

When a test bar is subjected to a tensile pull, the stress on any plane normal to the direction of pull is one of pure tension tending to pull

the atoms on one side of the plane farther away from those on the other. On all planes that are not perpendicular to the axis of pull the direct tensile stress can be resolved into two components; one normal to the plane and one along the plane. Thus, if the ellipse EF (Fig. 33) is a plane in a tensile test-bar of circular cross-section, the tensile pull P can be resolved into two components, OH normal to the plane, and OS along the plane. The stress normal to the plane tends to pull the atoms on one side of the plane farther away from those on the other, while the stress along the plane tends to produce movement of the material on one side relative to that on the other. Thus, under the pull P , the metal on the left-hand side of EF would tend to move in the direction OS while that on the right-hand side would tend to move in the direction SO . The component of the direct stress that acts along any plane in the test-bar is the shear component. This is the stress that produces permanent deformation, for it involves movement of the constituent parts of the bar relative to each other.

When P is the load on the test-piece, A the original cross-sectional area, and θ the angle between the normal to the plane and the axis of the test-piece, then the stress normal to the plane is given by

$$N = \frac{P}{A} \cos^2 \theta$$

and the shear component by

$$S = \frac{P}{A} \cos \theta \sin \theta.$$

$ABCD$ (Fig. 33) is a longitudinal plane through the test-bar and contains the axis of pull and the normal to the plane EF . When the direct stress is resolved into two components as above, the shear direction is OS which also lies in the longitudinal plane $ABCD$. If the shear com-

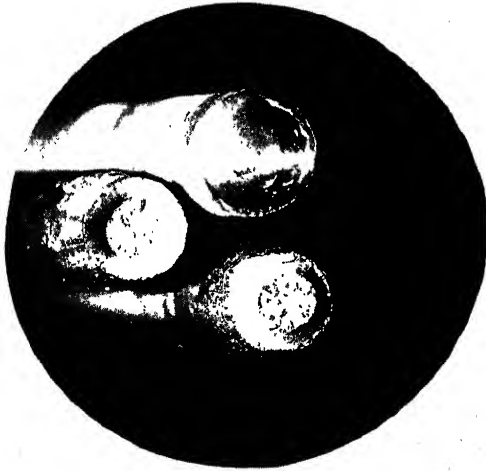


FIG. 34. Top: torsion fracture. Bottom: cup and cone fracture.

ponent in some other direction along the plane EF is required, say in the direction OK , it is given by the equation

$$S = \frac{P}{A} \cos \theta \sin \theta \cos n,$$

where n is the angle between OK and OS .

The resolved shear in the direction OK is less than that in the direction OS ; consequently, on any plane through the test-bar the resolved shear is greatest in the direction that lies in the same longitudinal plane as the normal to the shear plane and the axis of pull.

Confining attention to the resolved shear in the direction OS (i.e. in the longitudinal plane containing the normal to EF and the axis of pull), it may be said that this is a maximum when the shear plane makes an angle of 45° with the axis of pull. Thus, if θ in Fig. 33 is 45° , OS is the direction of maximum resolved shear. In a brittle material with no directional properties fracture will frequently take place by shear along the plane EF in the direction OS . In a ductile material the conditions

are different. If the imaginary plane EF is kept constant and the test-bar is rotated, OS traces out a cone. Thus, the direction of maximum shear is not really along a plane, but along the surface of a 45° cone. When the applied force is sufficient to produce permanent deformation, this takes place by movement of the constituent parts of the bar with respect to each other along the surfaces of such cones. For this reason a circular bar remains circular while it deforms, and finally breaks with a cup and cone fracture like that shown in Fig. 34.

THE MECHANISM OF DEFORMATION IN METAL CRYSTALS

Elastic Deformation.

The atoms of which crystals are composed are maintained in their respective positions by a system of interatomic forces of attraction and repulsion. When no external forces are acting on the crystals the positions occupied by the atoms are those of equilibrium between the attractions and repulsions. When external forces are applied the atoms are forced either closer together or farther apart. As they are forced nearer together, the forces of repulsion increase more rapidly than those of attraction, as they are forced farther apart the forces of attraction decrease less rapidly than those of repulsion. Thus the atoms behave as if they were connected together by a system of springs and the stability of the lattice is maintained while the interatomic distances are altered. To produce a continuous elastic compression or expansion the applied force must be progressively increased, and this accounts for the relations between stress and elastic deformation. This kind of deformation distorts but does not destroy the lattice. The atoms may be forced nearer together in all directions as in hydrostatic compression, or nearer together in some directions and farther apart in others as in a tensile test, but they return to their equilibrium positions when the external force is removed. A crystal cannot remain in a state of elastic strain in the absence of forces producing the strain.

Permanent Deformation of Single Crystals.

Permanent deformation differs from elastic deformation in that a certain minimum stress is required to initiate it, and it involves movement of the constituent parts of the crystals with respect to each other. Once a crystal has been permanently deformed its space-lattice is no longer continuous throughout its volume. The change produced is irreversible, and although the crystal may be restored to its original external shape by the application of force in other directions, this results in a further change in the structure of the crystal, and not in the elimination of the change produced in the first instance. Thus the effects of repeated permanent deformation in opposite directions are additive.

Several methods are now available for producing individual metal

crystals of sufficient size to be subjected to mechanical tests. These will be described in the appropriate place. Meanwhile, attention may be directed to the behaviour of single crystals when permanently deformed. As already explained, this type of deformation involves relative movement of the constituent parts of the material concerned. In an isotropic material this movement is controlled by the resolved shear. In a single crystal, however, the regular arrangement of the atoms produces directional properties, and movement of the component parts is controlled by the relations between the resolved shear and the arrangement of the atoms. Stated briefly, these relations are as follows: Permanent deformation by movement of the component parts takes place by the parts slipping with respect to each other along the most widely spaced crystallographic planes and in the direction of the lines in which the atoms are most closely packed. In any given crystal there are several combinations of planes and directions of slip, and the resolved shear determines which will be involved.

In close-packed hexagonal crystals the basal planes, i.e. the set parallel to the base of the unit hexagonal prism (Fig. 6), are more widely spaced than any others. Slip therefore takes place on this set of planes. The lines of greatest linear atomic density are the digonal axes indicated by broken lines on the top surface of the unit cell in Fig. 6. Slip therefore proceeds in one of these directions. In face-centred cubic crystals the (111) planes are the most widely spaced and the [110] directions are the lines of greatest linear atomic density. There are four sets of (111) planes and each set contains three [110] directions as shown in Fig. 16. Slip may therefore take place along any one of these four sets of planes and in any one of the three directions lying in that plane. Furthermore, it may take place simultaneously on two sets of planes. In body-centred cubic crystals slip is not confined to planes of one type. The (110) planes are the most widely spaced and the others follow in the order (200), (112), (310), (222), (123). The [111] is the direction of greatest linear atomic density and slip always takes place in one of the four [111] directions. (110), (112), and (123) planes contain a [111] direction as shown in Fig. 39, but (200), (310), and (222) do not. Thus, slip can only take place on (110), (112), and (123) planes, of which there are 6, 12, and 24 sets respectively. Sometimes it takes place on one set, but in general it takes place on a combination of planes determined by the relations between the resolved shear and the [111] directions.

Slip in Zinc Crystals.

The permanent deformation of single crystals of representative metals may now be considered. In the close-packed hexagonal metal zinc, there is only one set of slip planes, and three directions of slip lying in these planes. If a wire containing only one zinc crystal is prepared, and the orientation of the crystal with respect to the axis of the wire determined, it is possible to discover by calculation which of the three possible slip

directions will be subjected to the greatest resolved shear when the wire is stressed in tension. Slip will then take place in this direction along the basal planes.

$ABCD$ (Fig. 35 X) is a longitudinal section through a portion of a single-crystal wire of zinc. This section contains the axis of the wire PP and the normal to the basal planes WW . The lines parallel to AB and DC represent the intersections of the basal planes with the longitudinal

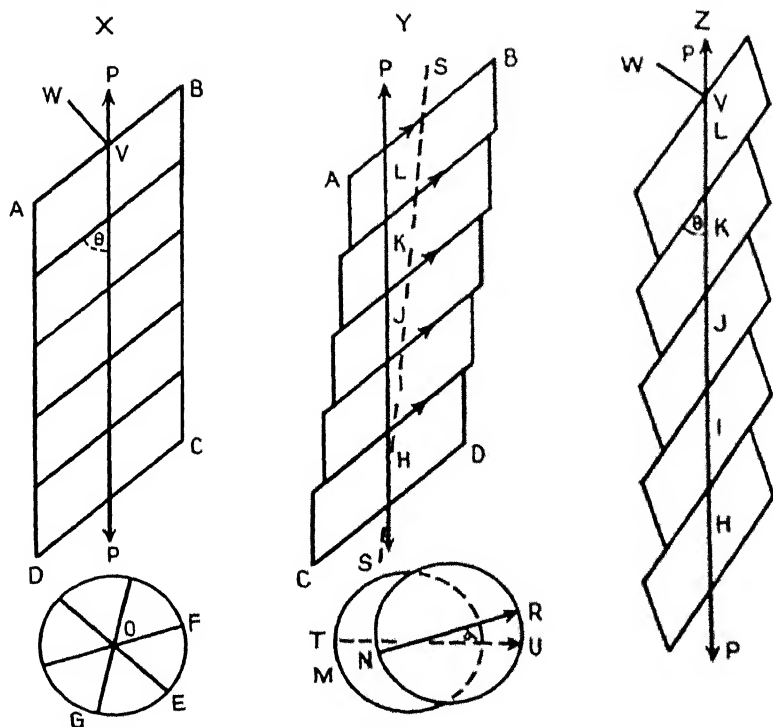


FIG. 35.

plane. GEE is a cross-section of the wire and OE , OF , and OG are the projections on to this cross-section of the slip directions contained by the planes AB , DC , &c. If the resolved shear in the direction OF is greater than that in the directions OG and OE slip will take place in this direction.

If it were possible to deform a single zinc crystal in such a way that the applied force had no effect besides promoting slip on the basal planes and in the appropriate direction, the conditions after a certain amount of slip had taken place would be as represented in Fig. 35 Y . Movement of the blocks H , I , J , K , L along the slip planes and in the slip directions would cause the crystal to deform in the direction indicated by SS on the longitudinal section and NR on the plan. At the end of the movement a cross-section of block H would occupy the position

indicated in plan by circle M , while a cross-section of block L would occupy the position indicated by circle N . But the direction of tensile pull is PP , and the ends of the wire are held in alignment by the grips of the testing machine. Consequently, the wire must extend in the direction represented by PP on the longitudinal section and TU on the cross-section. In other words it must extend in the direction of the tensile pull.

Now it is evident that if the crystal is to extend by slipping along the planes AB, DC , &c., in the direction OF (Fig. 35 X) and at the same time to extend in the direction of the tensile pull, some change must take place. The change that does take place is illustrated in Fig. 35 Z . As slip proceeds the angle between the slip planes alters so as to make these planes more nearly parallel to the direction of pull. At the same time the blocks between the slip planes rotate so as to bring the slip direction into the same longitudinal plane as the normal to the slip plane, i.e. the slip direction rotates from the position NR (Fig. 35 Y) to the position TU . Thus, by a change in the orientation of the crystal the slip plane and direction are brought into the position necessary for extension to take place in the direction of pull.

It follows from the above that as slip proceeds, the angle θ between the slip planes and the direction of pull must decrease, and so must the angle α between the slip direction and the longitudinal plane containing the normal to the slip plane. Thus, whatever the original orientation of the crystal, it will tend to attain a certain 'preferred' orientation after a certain amount of deformation has taken place. Owing to the way in which the blocks slip from the position shown in Fig. 35 X to that shown in Z , the diameter of the single-crystal wire decreases on the plane shown in these figures. In a direction perpendicular to this the diameter remains unaltered. Thus, an originally circular wire draws down to an elliptical ribbon.

In single crystals of zinc fracture takes place when the angle between the slip planes and axis of extension reaches a critical value which varies with temperature. At 20°C . it is between 10° and 20° , at 180°C . it is between 8° and 10° , and at 200°C . it is between 2° and 4° . The amount that a single crystal extends before fracture therefore depends on the original orientation of the basal planes relative to the axis of pull. Crystals in which the basal planes are perpendicular to the direction of extension are unfavourably oriented for slip, and under comparatively small loads failure takes place by cleavage on these planes. Crystals in which the basal planes make an angle of less than 20° with the direction of extension fracture after a small amount of deformation. Crystals of intermediate orientation deform easily, and to an extent that increases with the original angle between the slip planes and the direction of extension. At atmospheric temperature suitably oriented crystals can be drawn out to four or five times, and at 200°C . to seventeen times, their original length.

The extended copper-aluminium crystal shown in Fig. 36 closely resembles an extended zinc crystal. The steps produced by relative movement of the constituent parts of the crystal are clearly shown. These are known as slip-bands and are always produced on the surface of a deformed crystal. In single crystals subjected to tension, compression, or torsion, the slip-bands are visible to the naked eye, but in polycrystalline metals a microscope is required to observe them (Fig. 23). As explained in Chapter II, they are produced because slip does not take place on all the planes in the set involved. The spacing of planes in a set is such that there are between three and four hundred thousand in a linear millimetre, and if slip took place on them all, or even on a large proportion, the crystal could be extended hundreds of

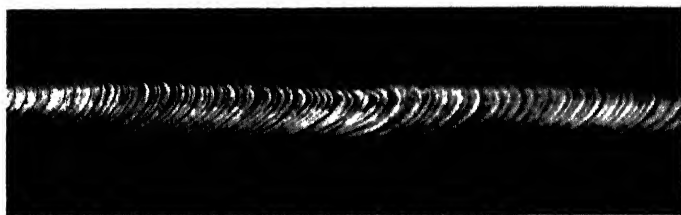


Fig. 36.

crystal. (Ehlers, *Distortion of Metal*.)

times its own length without surface steps of microscopically visible dimensions being produced. Actually, slip occurs on more or less equally spaced groups of crystallographic planes. The amount which takes place in one group is sufficient to produce a step of visible or microscopic dimensions, and the metal between the groups moves as an unaltered block. It is these blocks that are represented by *H*, *I*, *J*, *K*, and *L* (Fig. 35) and shown in Fig. 36.

Besides the process of slip described above, the deformation of zinc takes place by a 'twinning'. This phenomenon will be described later. Meanwhile, it must suffice to state that the total deformation that takes place in this way is small, although the reorientation of the lattice that results from 'twinning' may adjust a crystal to a position in which slip may occur to a greater extent.

Slip in Aluminium Crystals.

In face-centred cubic crystals the (111) planes, of which there are four sets, are the most widely spaced, and the [110] directions (i.e. the cube-face diagonals) of which there are six, are the lines of greatest linear atomic density. Each (111) plane contains three [110] directions as shown in Fig. 16, and in face-centred cubic crystals slip takes place on these planes and in these directions.

If a wire composed of one aluminium crystal is prepared and the orientation of the crystal with respect to the wire axis is determined,

the plane and direction of slip may be discovered by calculating the resolved shear in each $[110]$ direction on each (111) plane. Slip will begin in the direction in which the resolved shear is a maximum. As in the case of zinc, however, the crystal must extend in the direction of the wire axis, and in order that slip on the (111) plane and in the $[110]$ direction shall coincide with extension in the direction of pull the crystal changes its orientation to bring the slip plane and the slip direction into the requisite position. If there were no other planes on which slip could take place, this change in orientation would ultimately bring the (111) planes into a position approximately parallel to the wire axis and the

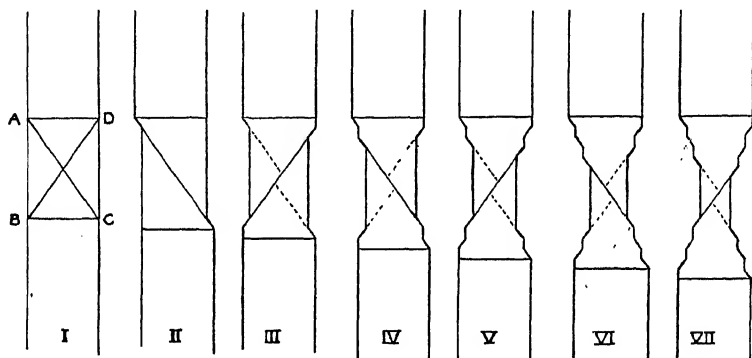


FIG. 37. Illustrating mechanism of deformation of a single crystal on two sets of planes. (Goucher, *The Philosophical Magazine*.)

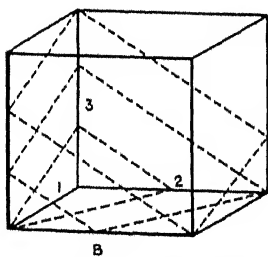
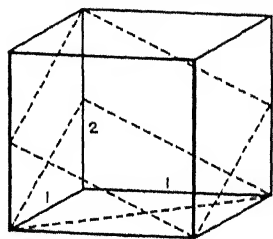
slip direction into the longitudinal plane containing the wire axis and the normal to the slip plane. But as the orientation changes, another set of (111) planes and another $[110]$ direction come into a position equally favourable for slip, and slip thereafter proceeds equally on both sets of planes. In this position the orientation of the crystal is such that the axis of pull bisects the angle between the two sets of slip planes and a $[112]$ direction is parallel to the wire axis. The manner in which slip takes place on two sets of planes is illustrated in Fig. 37. As in the case of zinc, an originally circular single-crystal test-bar becomes elliptical as a result of a reduction in diameter in the plane shown in Fig. 37 while the diameter at right angles to this remains unaltered.

Slip in α -Iron Crystals.

In body-centred cubic crystals the $[111]$ direction (i.e. the cube diagonal) is the line of greatest linear atomic density and has been definitely identified as the slip direction. No definite set of planes has been shown to function as the slip planes, and slip takes place on either of three sets of planes, or on various combinations of these according to the relations between the slip direction and the resolved shear. In α -iron and other body-centred cubic crystals the most widely spaced planes

that contain a $[111]$ direction are the (110) , (112) , and (123) . Two (112) planes are shown in Fig. 38 *A* and three (123) planes in Fig. 38 *B*. There are 6 sets of (110) , 12 sets of (112) , and 24 sets of (123) planes. All these sets contain a $[111]$ direction and in Fig. 39 one such direction is shown lying on one plane in one set of (110) , (112) , and (123) planes respectively. In this figure AB is the $[111]$ direction, $ADBC$ the (110) plane, $BEAH$ the (112) plane, and $BKAL$ the (123) plane.

If a wire containing one iron crystal is prepared and the orientation



g. 38. *A* (112) and *B* (123) planes.

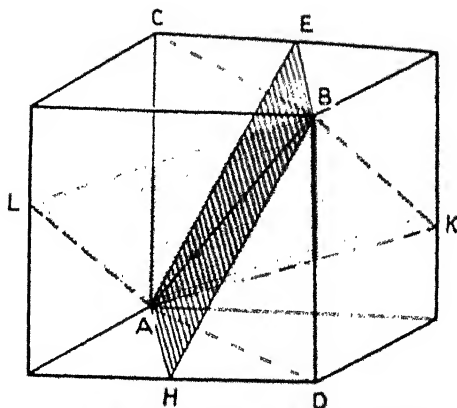


FIG. 39. AB is $[111]$ direction, $ADBC$ is (110) p
 $BEAH$ is (112) plane, $BKAL$ is (123) pla

of the crystal relative to the wire axis is determined, the resolved shear in each $[111]$ direction may be calculated. Slip will take place in the particular direction in which the resolved shear is a maximum. If the cube in Fig. 40 is a unit cell in a single iron crystal subjected to tension, PP the axis of pull, and AB the $[111]$ direction in which the resolved shear is a maximum, then slip will take place in the direction AB . This direction lies in any plane that can be obtained by rotating a plane about AB as axis. But the plane in which the resolved shear is greatest is the plane whose normal lies in the plane containing the axis of pull and the slip direction, i.e. the plane whose normal lies in the plane $ACBD$ (Fig. 40) (see Resolved Shear). Slip takes place on this plane and if it coincides with a (110) , (112) , or (123) set then slip takes place on that set of planes. If, however, the plane of maximum resolved shear does not coincide with one of these sets of crystallographic planes, then slip takes place simultaneously on two sets in such a way that the resultant plane of slip is the plane of maximum shear.

In hexagonal and face-centred cubic crystals slip takes place on definite sets of planes, and straight slip-bands are formed. In body-centred crystals straight slip-bands are formed when the plane of maximum resolved shear coincides with a particular set of (110), (112), or (123) planes. When, however, slip takes place on two sets simultaneously then wavy slip-bands are formed. Let, e.g., the slip-bands on a (100) face of an iron crystal be considered. On such a face the traces of all the (110), (112), and (123) planes may be drawn. If the trace of the slip plane (i.e. the plane of maximum resolved shear) coincides with one of the traces of the crystallographic planes the slip-bands will be straight. If it does not coincide, the slip-bands will be wavy.

Slip in Other Metals.

The other hexagonal metals, cadmium and magnesium, deform by slip in the same way as zinc, and the other face-centred cubic metals, copper, silver, gold, &c., deform in the same way as aluminium. It is doubtful, however, whether other body-centred metals deform in the same way as iron, and tungsten, e.g., seems to slip on (110) planes. The tetragonal crystals of tin deform by slip on (110) planes and in a [100] direction, while the rhombohedral metals, antimony and bismuth, do not appear to deform by slip but only by 'twinning'.

Attention has been confined to deformation in tension, but the mechanism of deformation is substantially the same when other types of stress, e.g. compression or torsion, are employed. A considerable amount of work has been done in studying the deformation of single metal crystals, and for further information *The Distortion of Metal Crystals* by C. F. Elam (21) and the numerous references contained in that book may be consulted.

General Consideration of Slip.

The atoms in crystals and the nuclei and electrons in atoms are all maintained in their relative positions by attractive and repulsive forces, and consequently an undistorted crystal may be regarded as an arrangement of particles maintained in position by a system of forces in equilibrium. Elastic deformation is consistent with this picture of a crystal, for the application of an external force tends to produce relative displacement of the atoms, and this invokes a restoring force which increases in magnitude with the applied force and brings the atoms back to their original positions when the external force is removed. But slip and its consequences could not be predicted from the simple picture of the crystal outlined above. Slip involves relative movement of the

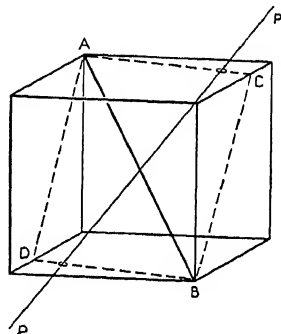


FIG. 40.

component parts of the crystal by a process of shear. The direction of slip coincides with a crystallographic direction of maximum linear atomic density. The plane of slip generally coincides with those crystallographic planes containing the slip direction on which the atomic density is equal to, or exceeds, that on any other plane containing the same slip direction. To this general rule relating to the plane of slip, α iron is an exception, and it may be that other body centred cubic metals will be found to resemble it.

If every crystallographic plane in the set on which slip is proceeding took part in the process, an enormous amount of deformation could take place without the production of microscopically visible slip bands. Such slip-bands are produced, however, and the distances between them are considerable in comparison with the distances between the crystallographic planes. This indicates that a relatively large amount of movement takes place on closely spaced groups of planes, while the intervening portions of the crystal are not affected. Slip bands first appear when the elastic limit is exceeded, and as the straining force is increased, fresh bands appear in previously undisturbed regions while the original bands increase in length. At any stage in the deformation the slip bands are not equally spaced, but nevertheless a fairly uniform distribution is usually observed. On single crystals of a given metal deformed at atmospheric temperature there is a fairly definite relation between the spacing of the slip-bands and the intensity of the resolved shear stress. This suggests that each slip-band represents a definite amount of slip. At temperatures other than atmospheric it appears that a similar relation holds when the crystals are subjected to a progressively increasing stress. Thus Yamaguchi and Togino (22) stretched aluminium crystals at the temperature of liquid oxygen, at atmospheric temperature, and at 500° – 600° C., and correlated the total extension with the appearance of the slip-bands produced. At the low temperature, however, the number of slip-bands produced by a given amount of distortion was greater than at atmospheric temperature, indicating that the amount of slip represented by each band was smaller. When crystals are deformed at elevated temperature by the prolonged application of a constant load, different conditions arise. Thus Hanson and Wheeler (23) found that aluminium crystals could be substantially deformed between 250° and 400° C. under a prolonged constant load without the appearance of slip-bands, because the number of slip planes was so great that the amount of slip on each was insufficient to produce visible bands.

The behaviour of metals in the tensile test shows that resistance to deformation increases as deformation proceeds, and the same phenomenon is encountered whenever metals are subjected to deformation at atmospheric temperature. A curve such as that shown in Fig. 27 does not take account of the reduction in area that accompanies deformation and suggests that the increase in resistance to deformation does not continue beyond the ultimate tensile stress. Curves such as *A* (Fig. 29) show,

however, that when the reduction in area is taken into account, the resistance to deformation increases with deformation until the metal fractures. These curves relate to polycrystalline test-bars, and their deformation differs in some respects from that of single crystals. The fundamental features are the same, however, and tests on single crystals also show that the resistance to deformation increases with deformation. Fig. 41 is a tensile load-strain curve for an aluminium single crystal and was obtained by Gough, Hanson, and Wright (24) by increasing the load in steps and allowing deformation to proceed with time at each step until no more would take place. The stress-strain curves obtained with

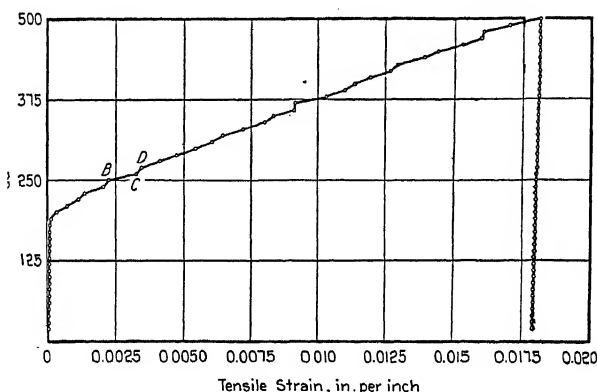


FIG. 41. Tensile load-strain diagram for aluminium single crystal. (Gough, *Trans. American Society for Testing Materials*.)

single crystals vary greatly with the orientation of the crystals relative to the direction of pull. When, for example, zinc crystals in which the basal planes are almost perpendicular to the direction of pull are tested, they fracture under low stress without any previous extension. Similar results are obtained when the angle between the basal planes and the axis of pull (Fig. 35) is less than 20° . If, however, the angle between the basal planes and the axis of pull is appreciably less than 90° , slip will take place readily, and proceed until this angle becomes about 20° . The greater the original angle, the larger the amount of extension that takes place before fracture, and in general the extension of zinc single crystals may vary between zero and 400–500 per cent. The other hexagonal metals behave in the same way as zinc. In single crystals of face-centred cubic metals there are four sets of slip planes and three directions of slip in each set of planes. Consequently, it is always possible for slip to begin on one set of planes and to continue until a second set comes into position for slip on conjugate planes as illustrated in Fig. 37. The stress-strain curves obtained with different single crystals of a face-centred cubic metal do not exhibit the same variations as those obtained with crystals of a close packed hexagonal metal, but nevertheless the shape of the curve alters with the original orientation of the crystal.

For all single crystals it is possible, however, to determine a curve that is independent of the orientation and which represents a fundamental characteristic of the metal concerned. This is the shear stress-shear strain curve. When a tensile stress is applied to a single crystal it is the resolved shear on the slip planes and in the slip direction that causes slipping to begin and to continue. As the orientation varies, the magnitude of the tensile pull required to produce a given value of the resolved shear also varies. If, however, the position of the slip planes and slip direction relative to the direction of pull is taken into account, the value of the shear stress producing slip can be calculated. If the shear stress obtained in this way is plotted against the amount of shear produced, a

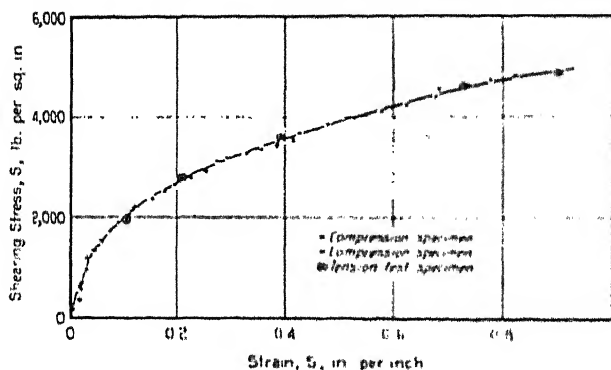


FIG. 42. Shear stress-strain curve for aluminium single crystal. (Clough, *Trans. American Society for Testing Materials*.)

fundamental curve which is independent of the orientation of the crystal or the type of stress applied is obtained. Fig. 42 (due to Taylor (25)) is a shear stress-strain curve for aluminium single crystals. Two crystals were subjected to compression and one to tension and shear stress plotted against shear strain. Although the method of stressing and the orientation of the crystals varied, the three curves coincide. Similar shear stress-strain curves have been plotted for groups of zinc and aluminium crystals of different orientation, and also for crystals of cadmium, tin, magnesium, gold, silver, copper, and nickel. In each case the same curve is obtained whatever the orientation of the crystal or the type of stress applied, and this is probably the only fundamental measurement that has yet been made in connexion with the mechanical properties of metals.

In Fig. 42 the shear stress-strain curve begins at O , i.e. the shear stress does not have to reach a critical value before the shear strain begins. Other investigators, however, have determined a quantity known as the 'critical resolved shear stress' below which no shear strain occurs. The value of this depends, however, on the accuracy of the methods used in detecting the beginning of strain, and it is doubtful

to what extent it is fundamental. All shear stress-strain curves resemble that shown in Fig. 42 in that they indicate that resistance to slip increases as it proceeds. They are therefore similar to ordinary tensile stress-strain curves of polycrystalline metals in that they reveal the phenomenon of strain-hardening. Comparison of the shear stress-strain curves of different metals shows that the face-centred cubic metals aluminium, copper, nickel, silver, and gold strain-harden at about the same rate, which is much more rapid than that characteristic of the hexagonal metals zinc, magnesium, and cadmium. On the basis of the behaviour of single crystals favourably oriented for slip these hexagonal metals appear to be much more ductile than the cubic metals, in that they strain-harden less rapidly and extend farther before they fracture. In polycrystalline aggregates, which represent the normal state of metals, the conditions are different, however, for whereas all the crystals in a face-centred cubic metal are situated so that slip can take place in one of the twelve directions, many of the crystals in a hexagonal metal are oriented in such a way that slip is practically impossible. Thus polycrystalline aggregates of face-centred cubic metals are much more ductile than those of hexagonal metals. When the shear stress-strain curve is determined for crystals of a given metal at different temperatures, it is found to become much steeper as the temperature is decreased, i.e. the rate of strain-hardening increases rapidly as the temperature is lowered.

Phenomena associated with Slip.

The mode of deformation of single crystals subjected to a tensile pull has been considered above, and it may now be said that this same process of slip on crystallographic planes and in crystallographic directions under the action of the resolved shear always occurs when metals are subjected to forces that produce permanent deformation. It is by the process of slip that single crystals change their shape when subjected to tension, compression, bending, or torsion; it is also by this process that the individual crystals in an aggregate respond to the deforming stresses in testing, service, and shaping operations, and when single crystals or aggregates are subjected to repeated stressing, slip again occurs. Slip is therefore one of the fundamental phenomena associated with the relations between metals and applied stress. So far it has been dealt with as if the component parts of the crystals glided over each other like cards in a pack, but it is obvious that much more complicated conditions must prevail, for while slipping is taking place the component parts retain their cohesion and the resistance to further slip increases. Furthermore, after a certain amount of slipping has taken place fracture begins.

A complete account of the mechanism of slip, should begin with a description of the forces of cohesion in metal crystals, then proceed to explain what occurs when one part of the crystal moves with respect to

another. It would account for the cessation of slip on the planes first involved, and explain why it is more difficult to produce slip on the planes that later become involved. Finally, it would describe in detail the relations between slip and fracture. It appears that it will be some time before such an account of the mechanism of slip will be available, and meanwhile it must suffice to describe some of the phenomena associated with slip in order to indicate the nature of the changes that are produced in the crystal structure. As slip occurs in the same way, and is associated with the same changes in crystal structure, whether single crystals or aggregates are studied, and whether these are subjected to single or repeated loadings in tension, compression or torsion or to cold rolling or drawing, what is said below applies to the deformation of metals generally, and is not confined to the particular conditions dealt with in previous sections. One of the most important phenomena associated with slip is strain-hardening, and attention may first be given to some aspects of this and to the earliest attempts to explain it.

Strain-hardening is a definite characteristic of metal crystals. It is exhibited in a pronounced degree at atmospheric temperature by crystals of iron and nickel, in a less pronounced degree by those of copper and aluminium, and in a still smaller degree by those of zinc, tin, and lead. At lower temperatures it becomes more and at higher temperatures less pronounced. Thus, lead at -480°C . behaves like iron at air temperature and iron at 800°C . behaves like lead at air temperature. This strain-hardening is difficult to explain, for it is plainly not a phenomenon that is confined to the planes on which slip is taking place. Thus, considering slip on one set of parallel planes: when the elastic limit is exceeded a certain amount of slip occurs on a certain number of planes; in further slip new planes will be involved, but nevertheless the stress must be increased before slip can take place on them. Thus, although new planes become involved, in each increment of slip the stress must be continuously increased in order to produce it. The fact that the resistance to deformation of the crystals as a whole is increased by slip on certain planes is even more clearly illustrated by considering the case in which slip begins on one set of planes and later takes place on two sets. In an aluminium crystal, for example, slip begins on the set of (111) planes in which the resolved shear in a [110] direction is greatest. As it proceeds, the crystal changes its orientation relative to the axis of pull and the resolved shear on other (111) planes increases. Slip will not begin, however, on a second set of (111) planes until the resolved shear in a [110] direction on these planes becomes equal to or greater than that on the planes already involved. Thus the resistance to deformation of planes on which no slip has taken place is increased to the same extent as that of the planes on which slip has taken place.

For many years the amorphous metal hypothesis was widely accepted as an explanation of strain-hardening. As explained in Chapter II, this hypothesis was first used to explain the surface hardening produced by

polishing. It was then argued that the relative movement of the parts of a crystal along a slip plane might be expected to produce conditions similar to those realized during polishing, and to cause the formation of an amorphous layer of metal along this plane. The amorphous material thus formed was supposed to be capable of existing both in the liquid and the solid state. When first produced in the liquid state it acted as a lubricant and facilitated slip, but when it solidified it assumed the hard resistant properties of glass and inhibited slip on the planes on which it had formed. On any particular plane a certain amount of slip could take place while the amorphous material was still liquid. Whenever it solidified, slip on that plane ceased. New planes were therefore required for the next increment of slip, and on these a further quantity of amorphous material was formed. Thus continued deformation was considered to produce a progressive increase in the amount of amorphous material, and the hardness resulting from deformation was attributed to the intrinsic hardness of this. As this hypothesis does not offer any explanation as to why the different planes which successively become involved in slip should offer a progressively increasing resistance to it, it does not explain this most important fact.

The development of preferred orientation is another phenomenon associated with slip, and it will be dealt with more fully in connexion with the deformation of aggregates. This is the term used to describe the condition reached after a substantial amount of deformation, when all the crystals in a polycrystalline metal tend to assume a similar orientation. In describing the deformation of single crystals of zinc, aluminium, and iron, it was shown that during the process of slip the orientation changes so that slip on the appropriate planes and in the appropriate direction may coincide with extension in the direction of pull. When a polycrystalline metal is deformed by rolling or wire-drawing, slip takes place on crystallographic planes and in crystallographic directions, but at the same time the crystals change their shape in conformity with the direction of application of the deforming force. To make these requirements coincide, the crystals change their orientation, and after a certain amount of deformation has been produced all the crystals in the metal attain a certain orientation known as the preferred orientation. This condition is not reached until after a substantial amount of deformation (*viz.* between 30 and 50 per cent. reduction in cross-sectional area by rolling or drawing), and is not observed to any appreciable extent in specimens deformed by simple tension, because fracture occurs before the necessary amount of deformation has been produced.

As preferred orientations are not developed until substantial amounts of deformation have been produced, while strain-hardening takes place most rapidly during the early stages of deformation, it is evident that the former is not the cause of the latter, and more subtle changes in crystal structure must be sought in order to discover the cause of

strain-hardening. In recent years a considerable amount of information on the nature of these changes has been obtained by the use of X-ray methods, but the conclusions reached by different investigators have not always been in agreement. It is impossible to describe and critically consider these investigations in this book, and for further information reference may be made to *The Distortion of Metal Crystals* by Elam, (21), *Crystalline Structure in Relation to the Failure of Metals* by Gough (26), and to papers by Gough and Wood (591) and Barrett (592). Meanwhile, some of the changes in crystal structure which have been discovered may be described without suggesting that the precise significance of these changes in relation to slip, strain hardening, and fracture is yet understood. The experimental methods used do not enable a distinction to be drawn between what is happening on the slip planes and what in the blocks between, but it may be inferred that the crystals as a whole are affected, although the changes may be more intense on and in the immediate vicinity of the slip planes.

In general, X-ray studies have shown that slip is accompanied by destruction of the regularity of arrangement that characterizes the undeformed crystal. Thus, after deformation has occurred, a single crystal or an individual crystal in an aggregate no longer consists of atoms arranged with absolute regularity on sets of smooth and parallel planes, but gives X-ray reflections which indicate that the orientation of the lattice changes from point to point so that the crystallographic planes are no longer smooth nor the successive planes in a set parallel. If within a given crystal deformation produces variations in orientation between one point and another, it is evident that either a substantial amount of elastic strain is induced or the lattice is broken up so that it consists of small fragments of different orientation partially separated from each other by minute flaws. It is doubtful, however, whether there is any real difference between these conditions, for it seems unlikely that the flaws will be of such magnitude as to represent a complete rupture of the cohesion between the atoms on opposite sides, and if not, there is nothing to distinguish a flaw from a region of high elastic tension. In any case, the X-ray results do not reveal whether the variations in orientation produced within an individual crystal are due to elastic strain or to the production of differently oriented fragments. Presumably definite rupture of the cohesion between the atoms is ultimately produced, but this represents the beginning of fracture rather than a phenomenon associated with slip.

Gough and Wood describe the changes in the crystal structure of a specimen of mild steel subjected to a tensile test as follows: Within the elastic range no change occurs in the initially perfect crystals. Between the elastic limit and the yield-point a few of the perfect grains show signs of destruction. 'Dislocation', i.e. the production of relatively large 'fragments' which differ only slightly in orientation, occurs, and a small proportion of 'crystallites', i.e. very small 'fragments' which

differ widely in orientation is produced. After the yield-point has taken place, every perfect crystal has been broken up into dislocated grains and a large number of crystallites have been formed. As deformation proceeds, dislocation continues, and larger amounts of crystallites are formed, and by the time the breaking-point is reached the metal consists entirely of randomly oriented crystallites. Barrett, who studied the changes in crystal structure by similar methods, considers that there is little justification for distinguishing between 'dislocation' and the formation of 'crystallites'. He concludes that the distortion of the crystals proceeds by the formation of areas of different orientation as a result of bending or perhaps of fragmentation, but he does not agree that there are two stages in this, i.e. the production of relatively large 'fragments' slightly tilted with respect to each other followed by the formation of small 'fragments' with greater divergences in orientation. His view is that the divergence in orientation between the different fragments increases progressively with deformation. Whatever may be the exact nature of the changes in crystal structure that accompany slip, it is evident that substantial changes occur and are in some way responsible for strain-hardening and associated with ultimate fracture.

The changes in crystal structure produced by deformation are accompanied by numerous changes in properties. Of these the most important is the change in resistance to deformation already described; but several others occur: (1) the electrical resistance is increased, (2) in ferromagnetic substances the susceptibility, permeability, and remanent magnetism are lowered, while the coercive force and hysteresis loss are increased, (3) the resistance to solution in acids and to corrosion is decreased, and (4) the density is decreased.

Twinning.

In the previous discussion of the structure of solid metals it has been assumed that the crystal structure is continuous throughout a crystal, and that a change in the orientation of the crystal structure denotes a crystal boundary. Twinned crystals are, however, exceptions to this, and exhibit changes in orientation within an individual crystal. In dealing with these it is necessary to explain in the first place how a twinned crystal is distinguished from two different crystals. This distinction is based on the fact that the two portions of a twinned crystal are crystallographically related to one another in such a way that the one may be derived from the other by a rotation on a certain plane about a certain axis and through an angle of 180° . The planes on which rotation may be supposed to have taken place are the twinning planes, and the axes about which rotation may be considered to have taken place are the twinning axes. Furthermore, the twins in a given crystal are separated from each other by crystallographic planes known as the composition planes which may or may not be the twinning planes. Owing to the fact that the portions of a twinned crystal are separated

from each other by a crystallographic plane, the boundary is straight, and under the microscope a twin usually appears as a parallel sided band running across the parent crystal. Examples of twins as seen under the microscope are shown in Fig. 93. In the absence of twins the structure shown here would be similar to that in Fig. 4, and the differently coloured bands crossing the crystals are twinned portions of these.

It must be emphasized that twins are not produced by the rotation of one part of a crystal with respect to another, but the relations between the orientations of twins are most easily illustrated by supposing this to take place. Attention will be given in the first place to these relations.

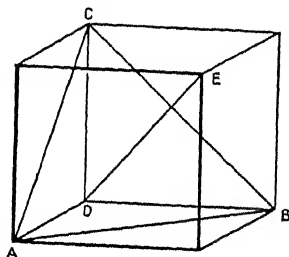


FIG. 43.

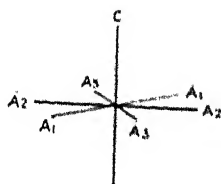


FIG. 44. Axes of hexagonal system.

The mechanism of twinning and the conditions under which twins are formed will then be described.

Twins are formed in all the well-known face centred cubic metals except aluminium, viz. in copper, gold, γ -iron, lead, nickel, platinum, and silver, in all the well-known hexagonal metals, i.e. zinc, magnesium, cadmium, and beryllium, and in those alloys of face-centred cubic and hexagonal metals in which these space-lattices persist. They are also formed in α -iron under certain conditions but have not been observed in the other body-centred cubic metals, e.g. chromium, molybdenum, and tungsten. Twins can also be produced in the tetragonal metal tin, and in the rhombohedral metals antimony and bismuth.

In face-centred cubic crystals twinning takes place on (111) planes and involves a rotation of 180° about a $[111]$ direction. Thus, referring to Fig. 43, twinning takes place on a plane of the type represented by ABC about an axis of the type represented by DE , and the relations between the orientations of the two parts are the same as would be obtained by rotating one part through an angle of 180° with respect to the other. In hexagonal crystals the twinning planes are of the $(10\bar{1}2)$ type and the twinning axes of the $[10\bar{1}2]$ type, and as the method of denoting planes in the hexagonal system has not yet been described, attention may be given to this. The unit cell in the hexagonal system is related to four axes taken in the order A_1, A_2, A_3, C in Fig. 44. The angles between A_1, A_2 , and A_3 in the positive directions are each 120° . C is at right-angles to the plane containing A_1, A_2 , and A_3 . The basal planes which

are parallel to the base of the unit hexagonal cell (Fig. 45) are (0001) planes, i.e. parallel to the axes A_1 , A_2 , and A_3 , and cutting C . Actually in the close-packed hexagonal system adopted by metals the basal planes are (0002) when their spacing is taken into account, but this notation is rarely used. The sides of the unit hexagon (Fig. 45) are (10 $\bar{1}$ 0) planes, i.e. dividing A_1 into 1 part, parallel to A_2 , dividing A_3 into 1 part and parallel to C . The six vertical faces of the hexagon are respectively (10 $\bar{1}$ 0), (01 $\bar{1}$ 0), ($\bar{1}$ 100), ($\bar{1}$ 010), (0 $\bar{1}$ 10), (1 $\bar{1}$ 00). The twinning plane (10 $\bar{1}$ 2) and the twinning axis [10 $\bar{1}$ 2] are shown in Fig. 45, the former being represented by $ABDC$ and the latter by FF . In α -iron, the only body-centred metal in which twins have been observed, twinning takes place on (112) planes about a [111] direction, and in the tetragonal metal tin it occurs on (331) planes about a [331] direction.

As already stated, twinning does not take place by rotation but by a process of translation similar to slip accompanied by some adjustment of the relative positions of the atoms. Slipping of the type previously considered cannot lead to twinning, for blocks of the crystal slide over each other without changing their relative orientation. To produce a twin every plane of atoms must be moved by a certain definite amount relative to its neighbour, so that a twin may be said to be formed when slip in a certain direction and of a certain magnitude occurs on a number of successive parallel planes in a particular set. When the requisite movement has taken place, the relations between the orientations of the twin and the parent crystal are the same as if a rotation had occurred, but the change is not produced in this way, nor is the plane separating the twin from the parent necessarily the twinning plane.

In metals that have not been deformed after solidification twins are not observed, and their formation is plainly dependent on mechanical deformation. Sometimes twinning is a conspicuous feature of it. In the metals antimony and bismuth, for example, no slip of the usual sort appears to occur and such deformation as does take place is by a process of twinning. In general, however, twinning is not a conspicuous feature of deformation. But this operation makes crystals unstable, and under suitable conditions of deformation, time, and temperature a process of recrystallization takes place as described in the next chapter. As a result of recrystallization a new generation of crystals is produced in place of the original deformed ones, and in all the well-known face-centred metals except aluminium, in the hexagonal metals, and in numerous alloys of these metals in which the face-centred cubic or hexagonal crystal structure persists, twins are a conspicuous feature

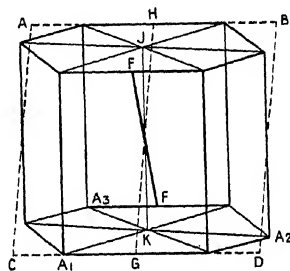


FIG. 45.

of the recrystallized metal. These become apparent after recrystallization, but all the evidence points to the fact that their presence is due to growth from a twin formed during deformation. This process will be described in the next chapter. For the time being it is sufficient to state that twins are not found in undeformed metals, that they are produced by deformation and are sometimes important features of this process, but that in general they do not become evident until recrystallization of the deformed metal has been brought about by suitable treatment. It must be further stated that sometimes the thermal stress set up during the cooling of a cast metal is sufficient to give rise to recrystallization accompanied by twinning, and in the case of metals like lead, tin, zinc, and cadmium, which can recrystallize at atmospheric temperature, the

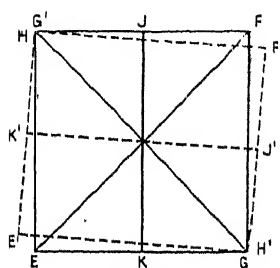


FIG. 46.

operations of grinding and polishing for microscopic examination may promote recrystallization and the formation of twins.

In the deformation of zinc and cadmium twinning plays an important part. In zinc the amount of extension that can take place as a direct result of twinning is only 7.39 per cent., but the process itself may bring the basal planes into a more favourable position for normal slipping. The plane $HFGE$ (Fig. 46) corresponds to $HFGF'$ (Fig. 45), i.e. it is

the plane containing the hexagonal axis JK , and the twinning axis FE . It is cut by the twinning plane ($ABDC$, Fig. 45) along the line HG . When a zinc crystal twins, the relations between the original and the new orientation are the same as would be obtained by rotating the unit hexagonal cell in Fig. 45 on the plane $ABDC$ about the axis FE through an angle of 180° . The effect of this is shown in Fig. 46 in which the plane $G'F'H'E'$, indicated by broken lines denotes the twinned position of the plane $HFGGE$. It will be seen that the hexagonal axis JK changes from the vertical position to the approximately horizontal position $K'J'$ and that the basal planes which were originally horizontal are rotated into a position only 4° from the vertical. In describing the deformation of zinc crystals it was explained that fracture occurs when the basal (slip) planes are brought into a position in which they make a small angle with the axis of pull. If, however, when the basal planes are approaching this position twinning occurs, they are rotated into a position in which they make a large angle with the axis of pull. Aable further amount of slip then takes place.

When one part of a crystal is twinned with respect to another it will, in general, present a different crystallographic plane to the attack of the etching reagent when a surface of the crystal is prepared for microscopic examination. Thus twins are easily distinguished under the microscope and are conspicuous features of the microstructure of deformed and recrystallized metals of the face-centred cubic and

gonal groups. Of the body-centred cubic metals the only one known to form twins is α -iron, for the production of which special conditions are necessary. When the metal is deformed by sudden impact, thin bands are revealed in the crystals when they are polished and etched. These are known as Neumann bands, typical examples of which are shown in Fig. 47. Their presence in a specimen of iron is definite evidence that it has been deformed by shock while in an unstrained condition, for slow deformation does not produce them, and they are not formed if the metal has been slowly strained before being subjected to shock. On the basis of the early studies of these bands it was concluded that they were

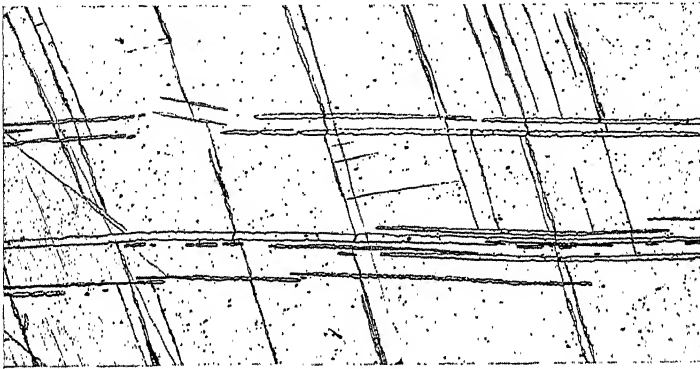


Fig. 47. Neumann bands in pure iron. $\times 250$.
(Pfeil, *Journ. Iron & Steel Institute*.)

twins, but definite proof was not obtained and later workers questioned the truth of this conclusion. As a result of the researches of Mathewson and Edmunds (27) and of Smith, Dee, and Young (28) it has now been definitely established that they are twins and they represent the most definite and best-known example of twinning in body-centred cubic metals. The twinning planes are (112) and the twinning axes [111]. Neumann bands have also been observed in γ -iron containing 18 per cent. of chromium and 8 per cent. of nickel in solid solution after the structure of which the metal formed a part had been destroyed by an explosion (29). Twins of the ordinary type have been produced in α -iron by McKeehan (30). ✓

THE DEFORMATION OF POLYCRYSTALLINE METAL

One object of the study of the deformation of single crystals is to obtain information that will lead to a better understanding of the deformation of aggregates, and although the latter is not capable of being dealt with in the same precise manner as that of single crystals the general factors involved are fairly well understood. The essential difference between a single crystal and a polycrystalline metal is that

in the former the crystal structure is continuous throughout, whereas in the latter its orientation varies from point to point. As deformation is a directional property and is thus related to orientation it is influenced to a marked extent by changes in it. Thus, although the deformation of the individual crystals in an aggregate closely resembles that of these crystals when deformed singly, the change in orientation between one crystal and another has a pronounced influence. This is generally referred to as the influence of the crystal boundaries, but it may equally well be described as the influence of changes in orientation or as the mutual effect of adjacent crystals.

When metals and alloys are considered as a whole, numerous types of crystalline aggregates have to be taken into account. The general factors involved in their deformation are not, however, very numerous. In so far as these relate to the deformation of aggregates containing more than one kind of crystal they will be considered in Chapter VI. For the time being attention will be confined to aggregates consisting of one kind of crystal. In this connexion all that has to be taken into account is the behaviour of the individual crystals and the mutual influence of crystals of different orientation.

Features of the Deformation of Single Crystals.

We have seen that a single crystal tends to deform by slipping on certain crystallographic planes and in certain crystallographic directions, in consequence of which it exhibits directional properties. When it is subjected to a tensile pull, it begins to deform as soon as the elastic limit is exceeded, and slip takes place along a set of planes in the particular slip direction in which the resolved shear is greatest. The conditions of the test demand, however, that the crystal shall extend in the direction in which it is pulled, and in order that this may be accomplished by slip on the appropriate crystallographic planes and in the appropriate crystallographic direction the crystal changes its orientation. Under other kinds of deformation similar conditions obtain and must be satisfied.

When single crystals of zinc of different orientation are pulled in tension their behaviour depends on their original orientation. If the slip-planes make an angle of over 85° or under 20° with the axis of pull, the crystals fracture without undergoing much extension. If, however, the angle between the slip-planes and the axis of pull is more than 20° and less than 85° , deformation takes place readily and to an extent that increases with this angle. Pronounced orientation effects are observed in zinc because there is only one set of slip-planes. In cubic metals the effects of orientation are less marked, for in face-centred crystals there are four sets of possible slip-planes and three possible slip directions in each, while in body-centred crystals there are four possible slip directions and an indefinite number of possible planes. Thus crystals of different orientation only exhibit moderate differences of strength in tensile tests,

though the elongation values may differ considerably. Carpenter and Elam (31) found the ultimate tensile strength of aluminium single crystals to vary between 2.8 and 4.08 tons per sq. in., while the elongation ranged from 34 to 86 per cent. on a 3-in. gauge length. Edwards and Pfeil (32) in tensile tests on twenty-five iron crystals of different orientation found that the ultimate strength varied between 9.38 and 15.38 tons per sq. in., while the elongation ranged from 31 to 53.65 per cent. on a 2-in. gauge length.

It has already been stated (p. 89) that the elastic limit, i.e. the stress at which permanent deformation begins, is a quantity which, in general, depends more on the sensitivity of the extension measurements than on the properties of the metal. Polycrystalline iron and many alloys of iron, and other hard body-centred cubic metals such as chromium, tungsten, and molybdenum, are partial exceptions to this rule, in that, although the observed elastic limit at ordinary temperatures may be lowered by increasing the sensitivity of the extension measurements, there is no doubt that within a certain range of stress they are elastic in their so-called primitive state (i.e. when not affected by previous deformation). In the case of copper and aluminium and their alloys the stress required to initiate the permanent deformation of polycrystalline specimens is small and is still smaller in single crystals. The same applies to an even greater extent to lead, zinc, and tin, and it has been shown that in single crystals of zinc permanent deformation begins when the resolved shear on the slip planes and in the slip direction reaches 94 gm. per sq. mm.

Single crystals of iron give stress-strain curves of the type shown in Fig. 27 and not of that shown in Fig. 32, i.e. they do not exhibit a definite elastic limit or yield-point. Deformation begins slowly, however, and up to a stress of about 2 tons per sq. in. the strain is proportional to the stress. Thus Edwards and Pfeil estimated the average elastic limit of single crystals of iron to be 2.19 tons per sq. in., while in their actual tests they obtained values varying with orientation from 1.72 to 2.69 tons per sq. in. The elastic limit of polycrystalline iron is from 7 to 8 tons per sq. in. Pfeil (33) obtained similar results for single crystals of iron tested in compression. The stress-strain curve was practically smooth, and all that could be deduced with certainty was that the limit of proportionality had been definitely exceeded at a stress that varied between 2.43 and 2.95 tons per sq. in.

The Effect of Crystal Boundaries.

The simplest type of crystal aggregate is that represented by a wire consisting of a row of crystals each of which occupies the entire cross-section. Such aggregates have been studied by Goucher (34) and Sykes (35) in tungsten and molybdenum wires respectively. In wires of this kind the crystal boundaries are approximately at right angles to the direction of pull. Deformation begins in the crystal most favourably

oriented for slip, and when this is strain hardened the crystal next most favourably oriented begins to deform and so this continues until all the crystals are taking part. The deformation of each crystal involves a relative movement of the component parts and some changes in orientation, but there is no relation between the changes taking place on opposite sides of a boundary. The crystal on one side tends to deform by slipping in a certain direction and by changing its orientation in a certain way. The crystal on the other side tends to slip in some other direction and to change its orientation in some other way. The two crystals cannot deform in a normal manner near the boundary and still remain in contact, and in consequence no slip takes place in its vicinity. Thus the original cross-sectional area is maintained in the neighbourhood of the boundaries, while the middle portions of the crystals draw down by slip. After an appreciable amount of deformation has taken place the originally uniform wire resembles a length of bamboo.

Several other investigators have studied the deformation of specimens containing two, three, or four crystals and have observed that none occurs near the boundaries. Aston (36), e.g., investigated the deformation of an aluminium specimen containing three crystals and found that the amount near the boundary was very small and that the effect of the boundary extended into each crystal to a distance of between 2 and 3 mm.

The Deformation of Aggregates.

Single crystals and wires composed of a row of crystals are unusual states of a metal. In the normal condition all crystals except those at the surface are completely surrounded by others. When such an arrangement of crystals is deformed, complicated conditions arise for (1) the metal as a whole must deform as determined by the applied force, (2) each crystal must deform in conformity with the deformation of its neighbours and of the metal as a whole, (3) each crystal must deform by slip on crystallographic planes and in a crystallographic direction, and (4) cohesion between the crystals must be maintained, otherwise fracture instead of deformation will occur. Conditions (1) and (2) are always satisfied, i.e. the metal deforms in a way determined by the applied force and each crystal changes its shape in conformity with the general change in shape of the metal. Condition (4) is generally satisfied and when intercrystalline cohesion breaks down, the metal is considered to have behaved abnormally, i.e. to have failed. In view of these facts the study of the deformation of polycrystalline aggregates becomes a consideration of the way in which the individual crystals must behave in order to deform in the required manner without losing contact with each other. It is clear in the first instance that deformation in the vicinity of crystal boundaries cannot be inhibited as in the case of a wire consisting of a row of crystals end on to one another, for when crystals are surrounded by others each must deform as a whole. It is also clear that

the change in the shape of any given crystal cannot be determined by the relations between its crystallographic planes and directions and the resolved shear, as in the case of single crystals. It must alter its shape in conformity with the resolved shear and the change in shape of its neighbours. In general, therefore, the individual crystals in an aggregate must behave as if they had no directional properties and as if their resistance to deformation near their boundaries was the same as elsewhere.

From a consideration of the general deformation of aggregates it may be shown that the crystals deform as if they had no directional properties, whereas from the study of single crystals it may be shown that the crystals have directional properties which exert a pronounced effect on their deformation. The question to be answered in connexion with the study of aggregates is how are these facts to be reconciled? The answer appears to be as follows: When a single crystal is deformed it slips uniformly along one or two sets of crystallographic planes in definite crystallographic directions. When a crystal in an aggregate deforms, slip still takes place on crystallographic planes and in crystallographic directions, but all possible sets of slip planes and all possible slip directions may be involved, and the planes and directions of slip may vary from point to point in the crystal. By slipping on a sufficient number of slip planes and in a sufficient number of directions, by changing its orientation to bring the slip-planes into a more favourable position, and by twinning, any given crystal in an aggregate may deform as demanded by the change in shape of the metal as a whole without departing from its characteristic behaviour of slipping on certain crystallographic planes in certain crystallographic directions.

While the above explanation of the deformation of the individual crystals in an aggregate may readily be applied to aggregates of cubic crystals in which there are numerous combinations of slip planes and directions, it cannot be so readily applied to hexagonal crystals with one set of slip planes and, actually, random aggregates of hexagonal crystals do not deform easily unless the temperature is such that recrystallization can accompany deformation. Once a preferred orientation has been developed by previous deformation, the same difficulty is not encountered. Thus, cast zinc is brittle at atmospheric temperature whereas hot-rolled zinc is ductile. This is further discussed in Chapter XVI.

It has been shown that in wires consisting of a row of crystals placed end to end no deformation takes place in the vicinity of the boundaries, because the directions in which slip should take place are different on each side of any given boundary, and so long as cohesion is maintained each crystal interferes with the deformation of its neighbour. In normal aggregates each crystal must deform as a whole and all the crystals must deform together in accordance with the change in shape of the metal. Thus deformation must take place in the vicinity of the boundaries just as elsewhere, and it follows, therefore, that no deformation of a crystal

can occur until the applied stress is sufficient to deform its neighbours and the material in the vicinity of the boundaries between them. In other words experiments with wires containing rows of crystals and specimens containing two, three, or four crystals show that deformation takes place less readily near boundaries, whereas the conditions in an aggregate require the crystals to deform as a whole, and in consequence the force required to produce deformation is that required to generate slip near the crystal boundaries. As the supporting effect of one crystal to another extends for some distance from the boundary—up to 2 or 3 mm. according to Aston—it is evident that in a normal aggregate the whole of each crystal must be to some extent prevented from deforming by the supporting action of its neighbours, and not only its immediate ones. Thus, the resistance to deformation of a metal increases as the average crystal size decreases, and this is one of the most important factors connecting the structure of metals with their mechanical properties.

It is clear that the deformation of an aggregate would be considerably facilitated if the crystals could move with respect to each other without losing cohesion, i.e. if slip within the crystals could be supplemented by intercrystalline adjustments. It is also clear that this adjustment would be controlled by different laws from those that apply to slip, and in particular it would be expected that deformation by intercrystalline movement would not be accompanied by an increase in resistance to further deformation. This is a difficult problem to investigate, but there is substantial evidence that the above change does take place and the general conditions of its occurrence may be stated as follows: When the conditions are such that the resistance to deformation increases with deformation and with decrease in crystal size, then, even if intercrystalline movement occurs, slip is the controlling factor. When, however, the conditions are such that resistance to deformation does not increase with deformation, and tends to decrease rather than increase with decrease in crystal size, then intercrystalline movement may be an important factor. The behaviour of iron, nickel, copper, aluminium, and their alloys in tests and deforming operations at atmospheric temperature shows that intercrystalline movement is slight under these conditions. Under prolonged loads at elevated temperatures, however, the resistance to deformation increases with increase in crystal size, there is a tendency for crystals to pull apart, and even for intercrystalline failure to occur, and it must be concluded that under these conditions an appreciable amount of intercrystalline movement does take place, although slip may still be the controlling factor. This is further considered in the next chapter.

The Effect of Crystal Size on Deformation.

In metals as ordinarily prepared and used each crystal is firmly bound to a number of differently oriented neighbours, and while intercrystalline cohesion is maintained, the change in orientation between one crystal

and another tends to retard deformation. This effect is quite pronounced even in specimens that contain only a few crystals, and it becomes increasingly greater as the number of crystals in a given volume of metal increases. Thus, resistance to deformation increases as the average crystal size decreases. It follows from this that a decrease in crystal size will be accompanied by an increase in the stress required to produce the first appreciable amount of permanent deformation, and this is particularly marked in the case of iron as shown below. That the rate of permanent deformation under an increasing stress should also diminish with a decrease in crystal size is not so evident, but it does diminish, and has to be explained. Two explanations are possible. One is founded on the idea that the resistance to deformation arising from the difference in orientation of the individual crystals is overcome gradually. The other is based on the view that when the individual crystals in an aggregate are deformed to a given extent they are strain-hardened more than if they were subjected to the same amount of deformation as single crystals.

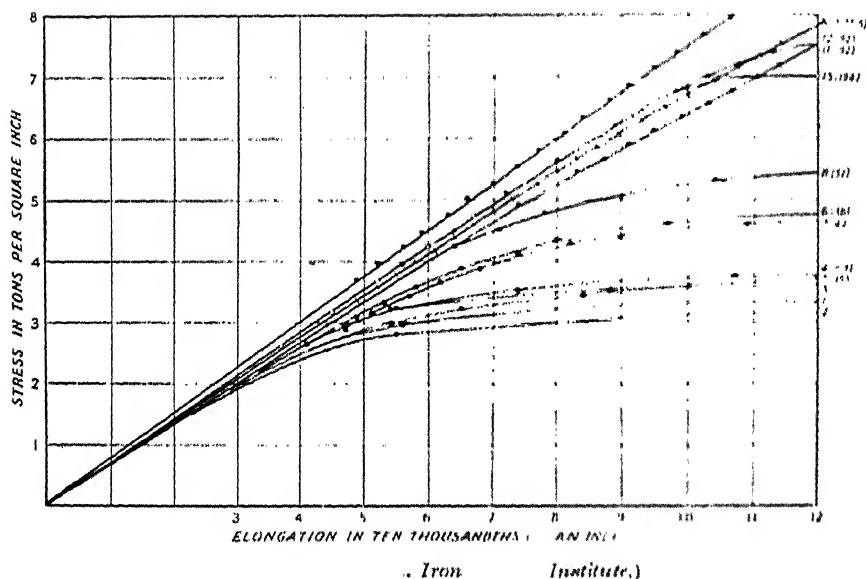
It is to be expected that the elastic limit of an aggregate will be higher than that of a single crystal, and it appears probable that if no permanent deformation could occur until the restraining influence of all the boundaries was overcome the elastic limit would be very high. Actually, however, the first small amount of permanent deformation is due to slip taking place in certain parts of certain crystals favourably situated for slip. Then as the stress is raised, more and more crystals become involved. Accordingly, deformation is accompanied by a progressive breaking down of the resistance arising from changes in orientation, and it is because of this that the stress-strain curve of polycrystalline metal is steeper than that of single crystals. When a point is reached at which all the resistance to deformation due to the boundaries has been overcome, the relations between stress and strain should be determined by the strain-hardening characteristic of the crystals, and if these are the same in aggregates as in single crystals there should be a marked change in the behaviour of the aggregate.

In a single crystal uniform deformation takes place on one or two sets of slip planes and the resistance to deformation increases in a definite manner as deformation proceeds. But in the individual crystals in an aggregate the deformation is not uniform, and all sets of slip planes may be involved in different parts of the same crystal. Thus, when a given change in shape is imposed on a crystal in an aggregate it may be strain-hardened to a greater extent than if it was deformed as a single crystal. Either of the above explanations would account for the fact that aggregates strain-harden more rapidly than single crystals and both may contribute to the observed phenomena. It appears, however, that the former is the more important.

Although the relative steepness of the stress-strain curve of aggregates is due to a progressive breakdown of the resistance of the boundaries

rather than to an increase in the rate at which the individual crystals strain-harden, both of these factors contribute to it, and when considering aggregates as a whole without regard to the behaviour of the individual crystal, it is quite justifiable to say that they strain-harden more rapidly than single crystals. This is an important characteristic for the rate of strain-hardening determines the ultimate tensile strength, the yield-point, the proof-stress, and the hardness. In aggregates of similar crystals the rate of strain-hardening increases as the crystal size

In those containing two kinds of crystals arranged in such a



way that the harder are distributed in a matrix of the softer crystals the rate of strain-hardening increases with an increase in the amount of the harder crystals, although they are not actually deformed. Thus any structural feature that promotes resistance to deformation tends to increase the rate of strain-hardening, and this principle is of great importance in connexion with the properties of alloys.

The work of Edwards and Pfeil (32) provides a particularly good illustration of the effect of crystal size on tensile properties. Fig. 48 shows the first portions of a series of stress-strain curves of iron test-bars containing different numbers of crystals, and the extension scale is very open in order to show the limit of proportionality. In specimens 1, 2, and 3 the average diameters of the crystals were 9.7, 7.0, and 2.5 mm. respectively. In the others the number of crystals per sq. mm. is shown in brackets alongside the number. It will be seen that the limit of proportionality is very low in the specimens containing large crystals, that it rises as the crystal size decreases and attains a maximum at 75.6

crystals per sq. mm., after which it decreases with decrease in the crystal size. Fig. 49 shows a continuation of the curves in Fig. 48 drawn on a smaller extension scale and illustrates the effect of crystal size on the yield-point. As this decreases, the yield-point stress and the extension at the yield-point increase to a maximum at 75.6 crystals per sq. mm., and thereafter decrease. The final portions of the load-extension curves

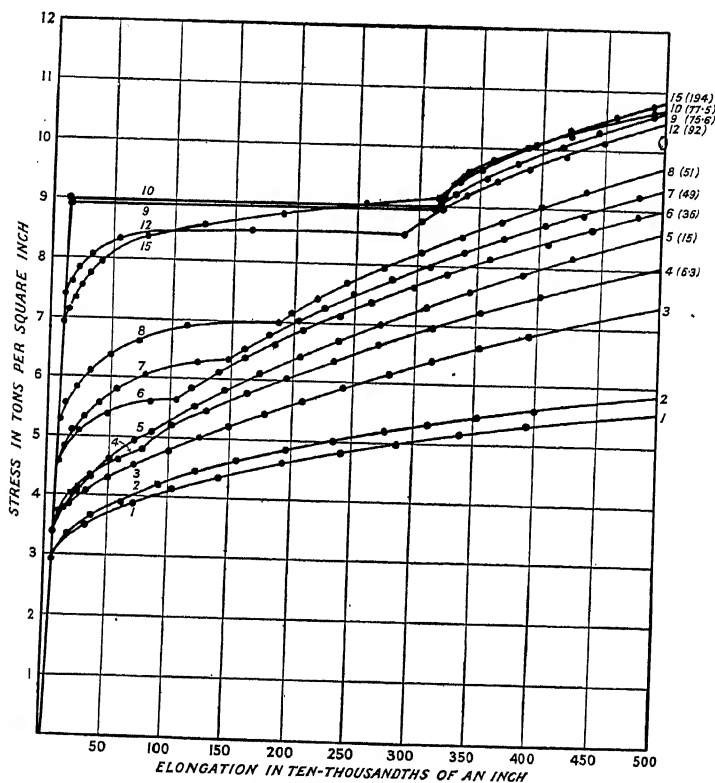


FIG. 49. (*Journ. Iron & Steel Institute.*)

are shown in Fig. 50, which shows the effect of crystal size on the maximum tensile strength.

The occurrence of a maximum on the curves connecting limit of proportionality, yield-point, and tensile strength, with crystal size, does not agree with what would be expected from the results of other work on the relations between hardness, &c., and crystal size. But varied treatments had to be performed to produce the different crystal sizes, and the decrease in the limit of proportionality, yield-point, and tensile strength which was obtained when the crystal size was reduced below a certain value is generally attributed to the changes in treatment. This view is supported by the fact that in the series of experiments

represented by Figs. 48 to 50 the maximum occurred at 76 crystals per sq. mm., while in a second series of experiments it occurred at 160 crystals per sq. mm.

One of the most commonly used methods of measuring the resistance (or rate of increase in resistance) to deformation is the hardness test, in

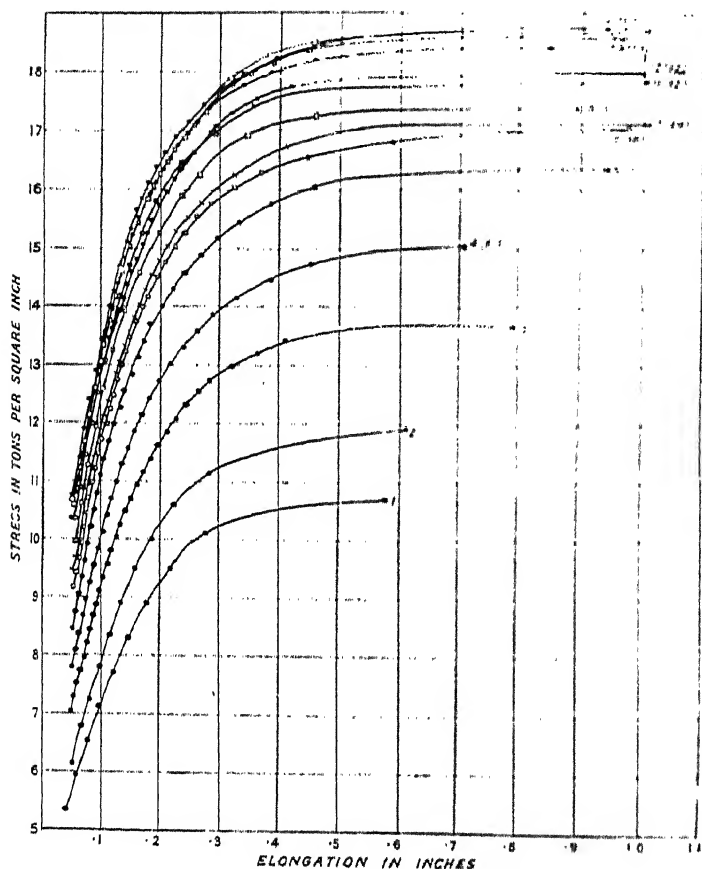


FIG. 50. (*Journ. Iron & Steel Institute.*)

which a hard steel ball, a diamond cone, or a diamond pyramid is pressed into the metal under a specified load and the depth or diameter of the resulting impression measured. The size of the impression made under given conditions decreases as the rate of strain hardening increases, and the result is taken as a measure of the hardness of the metal. Tests of this kind are described in Chapter VII. For the time being what is important is the effect of crystal size on the results obtained in a hardness test. Fig. 51 shows the results obtained by Wood (37) for

the relations between the average grain size and the hardness number of heat-treated steel. Similar curves have been obtained by other investigators using copper, brass, bronze, aluminium, &c., all of which show that the hardness increases as the crystal size decreases, the rate of increase in hardness becoming greater at smaller crystal size. The relations between hardness and crystal size shown in Fig. 51 may be represented by the equation

$$H = \frac{k}{S^2}$$

where H = hardness number, S = average diameter of the crystals, and k is a constant.

Preferred Orientation.

It has already been shown that when a single crystal is deformed, its orientation changes so as to bring the slip planes and slip directions into a certain position relative to the direction in which stress is applied. Thus, whatever their original orientation, all single crystals of a given metal tend to change it under deformation until a certain crystallographic direction is parallel to the direction of deformation. The same change occurs in aggregates, but it is not a conspicuous feature of deformation in the tensile test, because fracture takes place before or soon after the deformation reaches the stage at which the preferred orientation becomes pronounced, i.e. at a reduction in area of from 30 to 40 per cent. From a practical point of view, however, the deformation of metals is important because shaping by cold rolling and drawing depends on it, and in these operations drastic reductions are performed and definite preferred orientations are produced. The crystallographic direction that becomes parallel to the direction in which an aggregate is rolled or drawn is not necessarily the same as that which becomes parallel to the direction of pull when a single crystal is subjected to a tensile test. The stresses applied in these operations differ from those in the tensile test, and the behaviour of aggregates differs from that of single crystals. Nevertheless, the changes in orientation that occur under these different conditions depend on the same fundamental fact that in order to deform in the manner required by the applied stress by means of slip on crystallographic planes and in crystallographic directions a change in orientation must as a rule take place.

In wire-drawing the cross-sectional area is reduced by pulling the metal through a tapered hole in a die. The length of the hole between its smallest diameter (which determines that of the metal leaving the die) and the point at which its diameter is equal to that of the metal entering the die is known as the bearing. The angle at which the hole

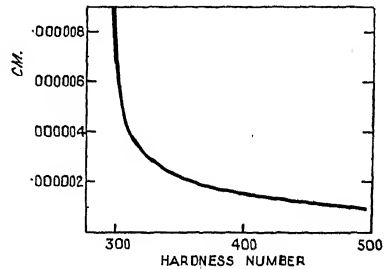


FIG. 51. (Gough, *Trans. American Society for Testing Materials*.)

tapers and the length of the bearing determine the amount of reduction in area produced by drawing through the hole. The operation of drawing the metal through one hole is known as a pass, and a given reduction in area may be produced either in a small number of heavy passes, i.e. drawing through a few holes each producing a large reduction in diameter, or in a greater number of light passes. In rolling the cross-sectional area is reduced by the pressure of the rolls, and whereas in wire-drawing it is usual to start with a round rod and draw round wire, by means of rolling numerous kinds of deformation may be produced. A round or rectangular bar may be reduced in area without changing the shape of the cross-section, a rectangular bar may be rolled to a round, a bar may be rolled into a strip or into a sheet by rolling in different directions, and so on. In view of the fact that the effect of wire drawing depends on the total amount of reduction and the number of passes used, while that of rolling depends on these factors and also on the relations between the original and final shape, it is not to be expected that all investigations on the effect of these operations will lead to the same conclusions. For the present purpose, however, what really matters is the fact that a preferred orientation is developed in all cases.

When a single crystal of aluminium is subjected to a tensile test it tends to approach a limiting position in which a $[112]$ direction is parallel to the axis of pull. If a bundle of single crystal wires of aluminium was subjected to a tensile test, a $[112]$ direction in each would tend to become parallel to the axis of pull. Thus a particular direction in each crystal would be parallel to the straining axis, but otherwise the orientations would vary. If, e.g., a unit face-centred cube is placed with a $[112]$ direction parallel to the direction in which the crystals are extended, then the unit cells in the crystals may be oriented in any position that this cube would pass through when rotated about this $[112]$ direction. This is the kind of preferred orientation developed in wires, and the X-ray reflections obtained from a heavily deformed wire resemble those which result when a single crystal is rotated about the preferred direction. The reflections are not the same, however, for although all the crystals in the wire tend to attain the preferred orientation, the deviations from this ideal position are always appreciable.

In tensile tests of single crystals of body-centred metals a $[110]$ direction tends to become parallel to the straining axis. When polycrystalline wires of these metals are drawn, a $[110]$ direction in each crystal tends to become parallel to the direction of drawing. In tensile tests of single crystals of face-centred metals a $[112]$ direction tends to become parallel to the straining axis, and when polycrystalline wires of these metals are drawn, a $[111]$ or a $[110]$ direction tends to become parallel to the direction of drawing. $[111]$ is the principal direction, but $[110]$ also tends to occur. Thus Schmid and Wassermann (38) found that in aluminium, copper, gold, and silver the proportion of crystals

that adopted [111] and [110] directions in their preferred orientation was as follows:

<i>Metal</i>	<i>Percentage of crystals with</i>	
	<i>[110] parallel to wire axis</i>	<i>[111] parallel to wire axis</i>
Aluminium . . .	0	100
Copper	40	60
Gold	50	50
Silver	75	25

In tensile tests of single crystals of hexagonal metals a $[10\bar{1}0]$ direction tends to become parallel to the straining axis. The deformation of polycrystalline metal is complicated by twinning and it appears that in zinc and magnesium it is a $[0001]$ direction that becomes parallel to the wire-axis in wire-drawing. $[0001]$ is the vertical axis of the unit hexagonal prism, while $[10\bar{1}0]$ lies in the basal plane between A_1 and \bar{A}_3 and is normal to the face $[10\bar{1}0]$. The extent to which the preferred orientation is developed in wires varies with the distance from surface to centre. Thus Schmid and Wassermann (38) found that the angle between the preferred direction and the wire axis decreased towards the centre, and Wood (39) found that a preferred orientation might occur in the core of a wire and not in the surface layers. Whereas wire-drawing tends to develop a preferred orientation in which a crystallographic direction is parallel to the wire axis while the orientation is otherwise random, rolling into foil tends to produce a preferred orientation in which one crystallographic direction is parallel to the rolling direction and a crystallographic plane is parallel to the rolling plane. The results that have been obtained in the study of the 'texture' of rolled metals exhibit more variation than those obtained in the study of wire. These results are summarized in the following table compiled by Gough (26):

TABLE 16
Preferred Orientations produced by Rolling

<i>Crystal structure</i>	<i>Metal</i>	<i>Direction parallel to rolling direction</i>	<i>Plane parallel to rolling plane</i>
Face-centred cubic . . .	{ Aluminium	[111]	(110)
	{ Copper	[112]	(110)
	{ Gold	[111]	(112)
Body-centred	{ α -iron	[110]	(100)
	{ Molybdenum	[110]	(112)
Hexagonal	Zinc	..	(0001)

THE MICROSTRUCTURE OF DEFORMED METAL

In considering the microscopically visible effects of deformation two aspects must be distinguished, viz. those seen on a surface polished before deformation and those seen in a section polished after deformation.

On a surface polished before deformation slip bands are found. They first appear when the elastic limit is exceeded and increase in number as deformation proceeds. As they are small steps on the surface they



FIG. 52. Hard-drawn steel wire (0.3°N C). $\times 400$.



Hard-drawn

are removed by polishing, and in specimens polished after deformation other evidence must be sought. In such specimens one of the most easily observed consequences of deformation is the change in shape of the crystals. Owing to the fact that the crystals in an undistorted metal do not have a very definite form, a small change in shape is not visible under the microscope. Thus in those parts of a tensile test-piece that

are not involved in the local extension the change in shape of the crystals is not apparent, and the same applies to metals that have been slightly reduced in cross-section by rolling or drawing. In the necked portion



FIG. 54. Hard drawn steel wire (0.75% C). $\times 100$.



FIG. 55. Hard drawn steel wire (0.75% C). $\times 430$.

of a tensile test-piece, however, the crystals are drawn out into elongated forms, and in general in metals deformed by tension, compression, or torsion, and in such operations as rolling, drawing, extruding, pressing, &c., the change in shape imposed on the metal is revealed by characteristic changes in the shape of the crystals.

Figs. 52 to 55 show the structure of two different kinds of steel wire

produced by a considerable amount of cold drawing. The specimen illustrated in Figs. 52 and 53 consists of two constituents, ferrite which is soft, and is essentially the same as the pure iron shown in Fig. 3, and pearlite which is harder and is the dark constituent in these figures. The specimen illustrated in Figs. 54 and 55 consists entirely of the constituent pearlite which, as explained in Chapter XI, is composed of alternate plates of ferrite and iron-carbide.

The changes in the structure of the crystals that result from deformation are not without influence on their appearance when polished and etched, and in addition to the fact that the grains have been elongated there is clearly a marked difference between the contorted ferrite crystals in Figs. 52 and 53 and the smooth crystals in Fig. 3. During deformation the individual crystals in an aggregate undergo slip which is more severe in some parts of the crystal than in others. This slip is accompanied by a kind of destruction of the crystal lattice which involves the breaking up of each individual crystal into 'fragments' of different orientation, and in many cases twinning also occurs. After moderate amounts of deformation, lines appear on the etched surfaces of crystals. These are known as deformation lines, and in certain cases have been shown to be twin bands. It is probable, however, that such lines may be formed in other ways by the concentration in certain regions of slip and its consequences, but the relations between the microscopic and X-ray characteristics of deformed metals have not been intensively studied. When the deformation is severe the effects of the alterations in crystal structure become very pronounced and it is sometimes impossible to distinguish the original crystals. The metal then appears like a distorted homogeneous substance.

Flow-lines.

Discussion of the mechanism of distortion has so far been confined to the behaviour of the individual crystals and the effect of the boundaries between them. These are the basic factors involved, but other aspects are also important. Thus a polycrystalline metal when subjected to the action of a force deforms as a whole as if it were an isotropic substance, and certain features of its behaviour can be considered without reference to the changes taking place in the individual crystals. If a tensile test-piece of iron or low-carbon steel is polished and stressed to the yield-point fine, dull lines appear on the surface as soon as the metal begins to deform. These are known as 'Lüder's-lines' or 'flow-lines' and appear in the first place near the points where the test-piece begins to enlarge at the ends, as shown in Fig. 56. Then as the extension at the yield-point proceeds they appear in increasing numbers until the whole surface is covered and separate lines cannot be distinguished. Careful examination of the polished surface of tensile test-pieces on which flow-lines have been developed reveals that they are actually slight depressions on the surface. When developed by compression they are small

ridges. On unpolished surfaces they may also be observed provided that the surface is covered with a layer of oxide formed during heating or hot-working, for the oxide flakes off where the lines appear.

Whatever type of stress is applied the flow-lines that appear at the yield-point coincide approximately with the directions of maximum shearing stress, and their formation is due to the fact that the distortion is not uniform. Thus, when a tensile test-piece is stressed to the upper yield-point sudden deformation takes place in certain layers and the load sustained by the specimen decreases. These layers are parallel to the directions of maximum shearing stress and the flow-lines are their traces on the surface of the specimen. Once the yield begins, deformation proceeds under an approximately constant load, and the process continues as follows: the layers that deform in the first instance are hardened by it so that the resistance to deformation tends to increase, but as soon as the load applied is slightly increased deformation takes place in new layers, and the load sustained by the specimen drops again. These new layers are strain-hardened and the metal can sustain an increased load until a further set of new layers begins to deform. Thus during the rapid yielding characteristic of iron and its alloys the lower yield-point stress is not really constant but fluctuates over a certain range as successive layers are deformed and strain-hardened.

The behaviour of a polycrystalline test-bar of iron at the yield-point resembles slip in a single crystal except that in the former the distribution of the flow-lines which take the place of slip-bands is due entirely to the shearing stress and not to the relations between this and the structure of the specimen. Furthermore, whereas the formation of slip-bands in a single crystal results in strain-hardening of the crystal as a whole, the formation of flow-lines does not affect the material not contained in the layers concerned. Flow-lines are not formed in other metals, but this does not necessarily mean that the distortion of these is

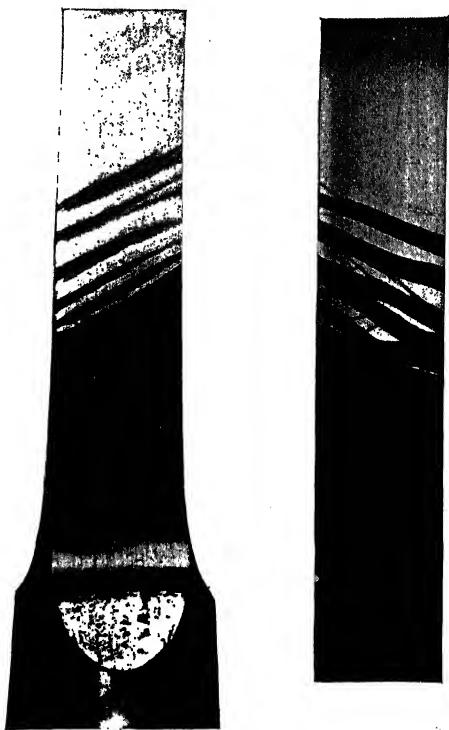


FIG. 56. Lüder's lines. (Körber, *Journal of the Institute of Metals*.)

For some reason polycrystalline iron at temperatures below 350° C. does not undergo substantial deformation under static loads until the applied stress is much higher than should be required to deform it. It displays a kind of mechanical hysteresis that does not appear when repeated stress is applied. Once the inertia of certain layers has been overcome they tend to deform readily under a stress much lower than that required to initiate deformation, but as they deform, these layers are strain-hardened and so at the lower yield-point a balance is reached between strain-hardening and the decreasing stress. In other metals distortion begins at a low stress and although it may be confined in the first instance to certain layers, the extent to which these are deformed relative to neighbouring layers is too small to be observed.

As the distribution of flow-lines in specimens stressed in tension and compression coincides with the direction of maximum shear, the study of those produced under complicated stresses provides important information on how these are distributed in the metal. For this purpose, however, the surface effects are inadequate, and some method of detecting flow-lines in a metal that has been sectioned and polished after deformation is required. The first successful method of revealing flow-lines by etching was developed by Fry and is described as follows by Berglund (16):—After straining the metal is heated to 200–250° C., for 30 minutes, then polished as usual and etched for 1–3 minutes in one of the following solutions:

For microscopic examination Fry's No. 3 reagent.	{ Cupric chloride	5 gm.
	{ Hydrochloric acid	40 c.c.
	{ Water	30 c.c.
	{ Ethyl alcohol	25 c.c.
For macroscopic examination Fry's No. 4 reagent.	{ Cupric chloride	90 gm.
	{ Hydrochloric acid	120 c.c.
	{ Water	100 c.c.

When taken out of the solution the surface is rubbed with powdered cupric chloride on a piece of cloth until the flow-lines appear clearly. It is then wiped, washed with alcohol, and dried. An alternative etching reagent has been proposed by Meyer and Eichholz, viz. cupric chloride 6 gm., ferric chloride 6 gm., hydrochloric acid 10 c.c., and ethyl alcohol 100 c.c. This reagent is weaker than Fry's and longer times of etching are required. The subject of strain-etching is dealt with in some detail by Turner and Jevons (40), Jevons (41), and Fell (42).

The study of the flow-lines on etched sections of steel has been used extensively in investigating stress distribution, e.g. (1) in rolling, drawing, pressing, &c., (2) in various shapes subjected to tension, compression, torsion, and bending, and (3) in cylinders under pressure, &c. It has also been used in the investigation of the stress-distribution round holes and notches. This aspect of deformation as an aid to stress analysis is discussed in detail by Nádaï (43) and as applied to rolling and drawing by Körber (44). One illustration will suffice for present purposes.

Fig. 57, due to Körber, shows the theoretical distribution of flow-lines in a flat test-piece pressed on both sides by a narrow-faced tool. The series of sketches *a*, *b*, *c*, and *d* represents the effect of increasing pressure and show how this affects the metal at progressively greater depths. The shading round the flow-line system in *d* is intended to indicate that with

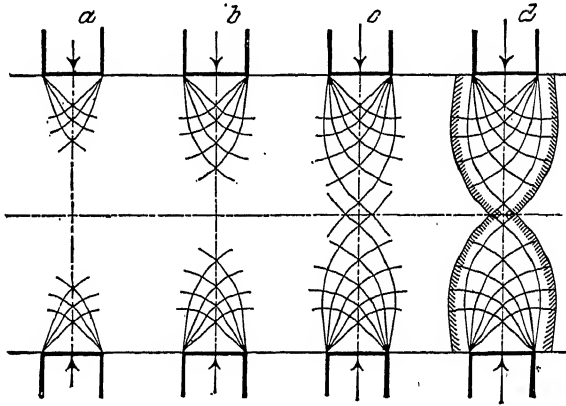


FIG. 57. Theoretical flow-lines in plate. (Körber, *Journal of the Institute of Metals*.)

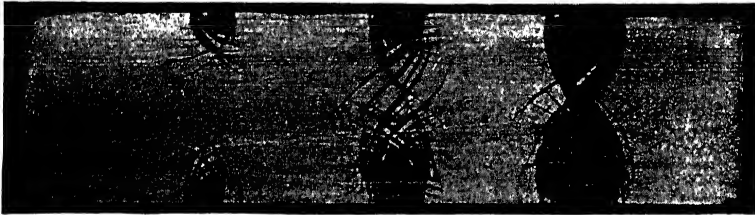


FIG. 58. Actual flow-lines in plate. (Körber, *Journal of the Institute of Metals*.)

heavy pressure all the metal within this region is deformed and individual flow-lines cannot be distinguished. Fig. 58 shows a longitudinal section of a test-piece deformed as described above and etched with Fry's reagent. The agreement between the actual and theoretical flow-lines is apparent.

FRACTURE

Deformation and Fracture in the Tensile Test.

In the foregoing sections the deformation of metals by the application of force has been considered, and it remains to deal with the other aspect of their response to force, namely, fracture. A certain mechanism is involved in this phenomenon, but this cannot be considered except in relation to the deformation that precedes and accompanies it, and to the nature, temperature of application, and conditions of application of the force.

Attention must be drawn in the first place to the relations between deformation and fracture in a tensile test at atmospheric temperature. In this test fracture occurs when the stress per unit of area attains a certain magnitude known as the breaking stress, and this multiplied by the cross-sectional area at the time of fracture gives the breaking load. In considering the relations between deformation, breaking stress, and breaking load we are concerned only with the type of curve represented by *A* (Fig. 29). This curve shows how the resistance to deformation per unit of cross-sectional area increases until fracture occurs. The ultimate tensile strength and the uniform extension depend entirely on the position of the point *d* at which the slope of the curve falls below a certain value. This point does not enter into the present discussion, nor does the ultimate tensile strength unless it happens to be the same as the breaking stress. What matters is that the resistance to deformation per unit of cross-sectional area increases progressively with deformation, and fracture occurs when it exceeds the breaking stress. The amount of extension that takes place before this occurs depends on the value of the breaking stress and the rate of strain-hardening.

Three aspects of the relations between deformation, breaking stress, and breaking load may be distinguished. In the first place, as explained above, a metal does not fracture in tension until the resistance to deformation per unit of cross-sectional area exceeds the breaking stress, i.e. the resistance to fracture per unit of cross sectional area. The resistance to deformation is increased to the requisite magnitude by the process of strain-hardening which accompanies extension, but while deformation results in an increase in resistance to it per unit of area it also causes a reduction in area. The second aspect of the relations between deformation and fracture is therefore the effect of reduction in area on the breaking load. The third aspect is the effect of deformation on the magnitude of the breaking stress.

In order to illustrate the connexion between resistance to fracture and resistance to deformation it is convenient to assume that three metals are available in which the breaking stress is the same while the resistance to deformation varies. If the breaking stress of one of the metals is less than the resistance to deformation that metal will fracture before any permanent deformation occurs. If the breaking stress of the other two metals is higher than the resistance to deformation, some deformation will precede fracture. If one of these strain-hardens rapidly, the resistance to deformation will exceed the breaking stress after a small amount of deformation has taken place. If the other strain-hardens slowly, the resistance to deformation will not exceed the breaking stress until a large amount of deformation has occurred. It is clear that, in the case of the metal in which no deformation takes place before fracture, the breaking load will equal the breaking stress multiplied by the original cross-section (neglecting the small reduction in area that may result from elastic extension). In the other metals,

however, owing to the deformation which takes place before fracture the cross-sectional area is reduced. Thus the breaking load decreases as the amount of deformation (measured by the reduction in area at the point of fracture) increases. It follows, therefore, that if a number of metals have the same breaking stress and different resistances to deformation (or, what amounts to the same thing, different rates of strain-hardening) then the metal that has the highest resistance to deformation will undergo the smallest amount of it and require the greatest load to break it, while the metal that has the least resistance to deformation will undergo the greatest amount of it and break under the smallest load.

In considering the results of tensile tests as ordinarily carried out it is possible to explain nearly all the observed phenomena without assuming any differences in the breaking stress of different metals. This is possible because the breaking stress is not measured, and the quantities that are measured, such as ultimate tensile stress, elongation, and reduction in area depend on the rate of strain-hardening, and are not appreciably influenced by the breaking stress. Thus in practice metals behave just like the three hypothetical examples described above. Those that strain-harden rapidly fracture before the cross-sectional area at the point of fracture is greatly reduced, whereas those that strain-harden slowly draw down to a fine point before breaking. This is in qualitative agreement with the assumption that they all have the same breaking stress. Differences in the breaking stress only become apparent in the tensile test when no appreciable amount of permanent deformation occurs.

Two aspects of the relations between deformation and fracture have now been considered, viz., the connexion between breaking stress and resistance to deformation and the effect of this on the breaking load. It remains to consider the third aspect, namely, the effect of deformation on the magnitude of the breaking stress, and this will be done in the next section.

Breaking stress.

In whatever way metals are fractured the rupture is gradual in that it begins at a certain point and extends over the cross-section. In a tensile test, fracture begins in the necked portion at a point on the axis of the specimen and spreads from there along the surface of a cone until rupture is complete. In a bending test it begins on the outer side of the bend and proceeds across the section, and in tests in which repeated stresses are applied in tension, bending, or torsion the fracture likewise begins at a point on the surface and extends from there. Figs. 59 and 60 show intermediate stages in the fractures produced in repeated stress tests.

It is evident from the above that two stages in fracture may be distinguished, viz. its initiation and its propagation. As the latter is better understood than the former it may be considered first. When any solid

containing a notch, crack, or other discontinuity is subjected to stress there is a concentration of this at the end of the crack or discontinuity, and the extent to which the stress is concentrated in this way increases with the sharpness or fineness of the discontinuity. In any case this concentration of stress tends to extend the discontinuity and it is this that accounts for the propagation of a fracture once it has been initiated. The extent to which stress is concentrated at the end of a discontinuity in an elastic solid can be calculated and is found to be very great. Thus, if such a solid contains any discontinuity capable of serving as the



FIG. 59. Fatigue cracks in wire. $\times 100$.

starting-point of a fracture, it may be ruptured by comparatively small stresses. In materials that are capable of permanent deformation the effects of discontinuities are less pronounced, for the capacity to deform results in a redistribution of stress at the end of the discontinuity and it is not so easily propagated. It is this that accounts for the fact that rock-salt is stronger above 200°C . than at atmospheric temperature. It also accounts for many of the phenomena observed in studying the behaviour of metals subjected to stress, and it can be said definitely that the capacity to undergo a certain amount of deformation increases the resistance to fracture. It has already been shown, however, that the ultimate tensile strength increases with increase in resistance to deformation and is, in fact, a measure of resistance to it. Thus the capacity to deform has two opposite effects. On the one hand, it tends to raise the strength by increasing the resistance to fracture, on the other, it tends to decrease the strength by facilitating reduction in cross-sectional area. The selection of a material that will deform to a sufficient extent to prevent easy fracture, and at the same time resist deformation to an extent sufficient to give a high ultimate tensile stress is one of the most

important problems in engineering design. If the conditions realized in service were the same as those obtained in the tensile test it would be easy to solve the problem, but the difficulty is to make allowance for the difference between tensile and other tests on the one hand and service conditions on the other. This will be discussed more fully in Part III. Meanwhile, one example may be given of the general relations between strength and resistance to deformation.

If a specimen of steel containing 0.7 per cent. of carbon is quenched in water from 850° C. its resistance to permanent deformation is very



FIG. 60. Fatigue crack in wire. $\times 100$.

great. When subjected to a tensile test it breaks under a small stress because its resistance to fracture is low. Reheating the steel to temperatures between 200° C. and 700° C. before testing results in a decrease in the resistance to deformation. The first effect of this is to raise the breaking stress which in hard material like this is the same as the ultimate tensile stress. On further decreasing the resistance to deformation by reheating at higher temperatures, deformation proceeds to such an extent that the point *d* on curve *A* (Fig. 29) is passed before fracture occurs. The ultimate tensile stress and breaking stress are then separated. Finally, on further decreasing the resistance to deformation the ultimate tensile stress begins to fall. Thus, if a series of specimens of a steel containing 0.7 per cent. of carbon is tested (1) in the water-quenched condition, and (2) after reheating at a number of temperatures between 200° and 700° C. a series of stress-strain curves like those shown in Fig. 61 is obtained. In the quenched condition the breaking stress coincides with the ultimate tensile stress and both are low (curve *A*). Reheating reduces the resistance to deformation and the breaking stress

and tensile stress increase (curves *B* and *C*). On further decrease in the resistance to deformation the ultimate tensile strength decreases (curves *D* and *E*).

We have just seen that the capacity for undergoing deformation tends to raise the breaking stress by retarding or preventing the development of minute discontinuities. As deformation proceeds, however, this capacity is gradually exhausted, and a metal that is ductile at the beginning of the test becomes progressively less so as the test proceeds. Thus continued deformation tends to bring an originally ductile metal into a condition in which it resembles a brittle material.

e straining, as in the tensile test, therefore has the effect of

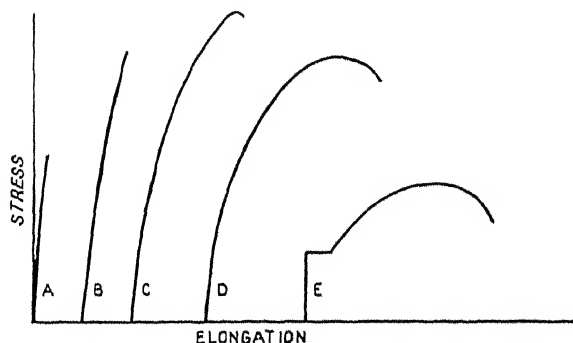


Fig. 61. curves of (tempered)

exhausting the capacity of the metal for deformation, and at the same time increasing the applied stress. At a certain point the combined effect of these conditions results in fracture, i.e. the metal is now sufficiently resistant to deformation to be incapable of resisting the propagation of a crack under the stress that is now applied. Thus we may say that fracture occurs when the resistance to deformation is greater than the breaking stress under the imposed conditions. This is one feature of the relations between deformation and the magnitude of the breaking stress. Besides resulting in strain-hardening, however, it is very probable that the changes in crystal structure which accompany deformation may be the cause of the formation of minute discontinuities which develop into fractures. Thus the reorientation which occurs in the crystals and leads to dislocation, fragmentation, and the formation of crystallites may eventually result in the generation of internal elastic stresses sufficient to produce flaws which are later extended into fractures. This is another feature of the relations between deformation and the magnitude of the breaking stress, but its importance is uncertain, for it has been established that brittle materials which do not deform, fracture readily by the propagation of discontinuities originally present or readily initiated, and the fracture of other materials may take place in the same way after their capacity

for deformation has been sufficiently decreased without the deformation being directly responsible for the initiation of the flaw.

The stresses required to rupture solids are very small in comparison with what would be expected from consideration of the forces of cohesion between the atoms, and it is generally supposed that this discrepancy is due to the existence of discontinuities which serve as the starting-point of cracks. The forces of cohesion between the atoms in metals cannot yet be calculated, and in any case, owing to the changes in crystal structure produced by the deformation that precedes fracture, it is difficult to discover the exact condition of the metal in which fracture begins. As an example of the discrepancy between theoretical and actual strength other materials may therefore be considered.

Rock-salt is a very perfect crystalline substance and large single crystals are easily obtained. As the crystals are of the ionic type, the force between the atoms can be calculated and values obtained for the properties that depend on them. Thus the modulus of elasticity, the surface tension, and the specific heat of rock-salt have been calculated and found to agree with experiment. At atmospheric temperature rock-salt is elastic to the point of fracture and according to calculation a single crystal subjected to tension in a [100] direction should break under a stress of 128 tons per sq. in. after an elastic extension of 14 per cent. In actual tests on rock-salt at atmospheric temperature it breaks under a stress of 0.128 to 0.320 tons per sq. in. after an extension of less than 0.1 per cent. The actual breaking stress may therefore be as little as a thousandth of the theoretical breaking stress calculated from the forces of cohesion. As already stated the strength of rock-salt is increased by testing at temperatures above 200° C. when some permanent deformation precedes fracture. Joffé (45) concluded that the low strength displayed by rock-salt in a tensile test was due to the initiation of fracture by surface discontinuities and he endeavoured to eliminate this effect by continuously dissolving the surface of the crystal undergoing test. In this way he obtained a breaking stress of 102 tons per sq. in. which is of the same order of magnitude as the calculated cohesion.

Griffith (46) also carried out a number of experiments that illustrate the discrepancy between cohesion and the strength obtained in a tensile test. He found that glass-fibres of 0.040 in. diam. had a tensile strength of 11 tons per sq. in. As the diameter of the fibre was decreased, the tensile strength increased, and a very fine fibre 0.00012 in. diam. had a tensile strength of 220 tons per sq. in. By extrapolating his results Griffith calculated a tensile strength of 720 tons per sq. in. for a fibre of zero diameter. This would then be the value of the absolute cohesion of the glass.

Joffé attributed the low strength of rock-salt to surface flaws while Griffith attributed the low strength of glass-fibres of appreciable dimensions to internal flaws. These explanations of the discrepancy between actual and calculated strength have been widely accepted and the

assumed flaws have been connected up with the idea of the mosaic structure. Other explanations are possible, however, especially where metals are concerned, and at the present time it is impossible to reach a final conclusion on the subject. It may be that the low strengths observed in practice could be adequately explained if cohesion was properly understood and if the distribution of stress was exactly known. At the same time, it is well known that surface or internal discontinuities facilitate fracture and it cannot be demonstrated that minute discontinuities are not an inevitable feature of solids. Whatever may be the true explanation of the difference between actual and theoretical strength

Griffith's experiments on the effect of diameter on tensile strength are of considerable importance and reveal an aspect of testing that should always be taken into account.

Wire-Drawing and the Tensile Test.

The curve *oafz* (Fig. 31) represents the result of a tensile test on annealed copper, i.e. copper that has been heated to eliminate any effects of previous deformation. The abscissa is the extension expressed as a percentage of the original length, while the ordinate

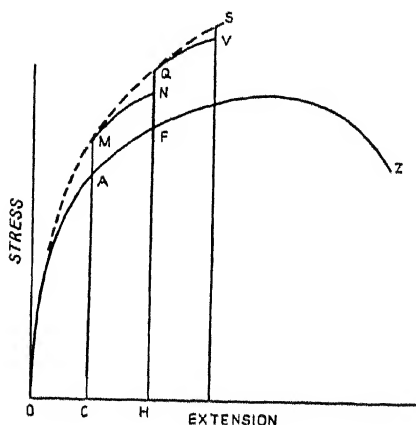


FIG. 62.

is the load divided by the original cross-sectional area. In describing this figure it was explained that if the load is progressively increased so that the portion *oa* of the curve is traced, the metal contracts elastically along *ac* when the load is removed. On again increasing the load the metal extends elastically along *ca* and then when it reaches *a* extension begins to follow the curve *af*. The same procedure may be repeated when the load-extension curve has been traced as far as the point *f* (Fig. 31) and in general the complete load-extension curve *oafz* may be obtained either by continuous loading or by repeated loading and unloading.

The curve *oafz* is reproduced in Fig. 62. If the load is increased to *a* and removed as described above, the cross-sectional area of the specimen will be permanently decreased as a result of the plastic extension *oc*. If the specimen is again loaded and the extension is plotted against the total load divided by the new cross-section, the curve representing the second loading will follow the course indicated by *cmn*. Marked plastic extension begins at the same total load as under the conditions represented by Fig. 31, but this is now being divided by a smaller area so that the stress at which it begins is actually higher, i.e. at *m* instead

of a . The curve $oafz$ shows the change in resistance to deformation of the cross-sectional area as a whole and takes no account of the reduction in cross-sectional area during the test. The curve $omqs$ shows the change in resistance to deformation per unit of actual cross-sectional area (i.e. it is the same as curve A , Fig. 29, except that the abscissa is extension instead of reduction in area). When the new cross-sectional area is determined after loading to a , the conditions change from those represented by $oafz$ to those represented by $omqs$, i.e. the stress producing the permanent extension oc rises from a to m because the area by which the total load is divided is decreased. When the load is further increased, however, the extension does not follow the curve mqs because the change in cross-sectional area is not being continuously measured. Once the point m is passed and further permanent extension begins, the actual cross-sectional area becomes less than that used to determine the stress. Thus the curve for the second loading follows the course cmn . If the cross-sectional area is again measured at n and the stress calculated on this new area, the stress-strain curve will again rise temporarily to the appropriate point on the curve $omqs$, i.e. to q .

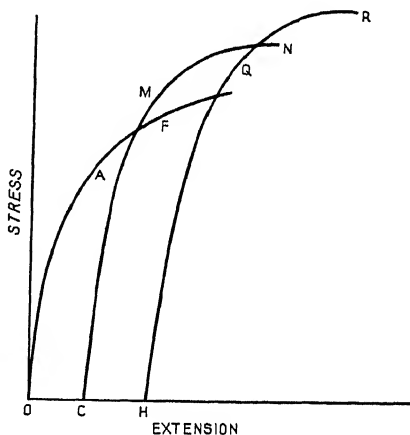


FIG. 63.

oaf (Fig. 62) represents the initial portion of the stress-strain curve of copper in its primitive condition. cmn represents the initial portion of the curve when the metal has been extended by the amount oc and the stress-strain curve is plotted on the basis of the reduced cross-sectional area. hqv represents the initial portion of the curve when the metal has been extended by the amount oh and the stress-strain curve is plotted on the basis of the reduced cross-sectional area. As already pointed out, however, metal that has been subjected to a given stress is not elastic up to that stress during a second loading. It undergoes much less permanent deformation during the second loading but an appreciable amount still takes place, so that the form of the three curves oaf , cmn , and hqv is actually as shown in Fig. 63.

The foregoing is the basis of what is known as work-hardening, i.e. increasing the resistance to deformation and the ultimate tensile strength by deformation prior to testing. It depends on the fact that the resistance to deformation per unit of actual cross-sectional area increases as deformation proceeds, so that, if, after a certain amount of deformation has been performed the new cross-sectional area is determined, and the stress is calculated on this, the metal appears to be harder than

originally. Curves like those shown in Figs. 31, 62, and 63, in which stress is plotted against extension, are, however, not very suitable for showing the effect of deformation on resistance to deformation. Once the maximum tensile stress is passed and local extension begins, the load sustained by the specimen starts to diminish, although the resistance to deformation per unit of actual cross-sectional area is still increasing, and the amount of deformation taking place appears to be quite small because the extension on a short length is divided by the whole gauge length. Curves such as those shown in Fig. 29 give a much better idea of the relations between deformation and resistance to deformation.

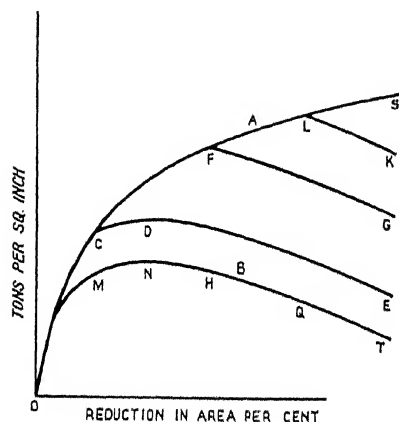


FIG. 64.

Curve *A* in Fig. 64 may be considered to represent a true stress-deformation curve of annealed copper, for the resistance to deformation per unit of actual cross-sectional area is plotted against the percentage reduction in area at the smallest cross-section. This curve indicates the rate at which the resistance to deformation increases with deformation. Curve *B* (Fig. 64), on the other hand, represents the type of curve obtained when the resistance to deformation of the cross-section as a whole is plotted against reduction in area, i.e. the ordinate is the applied load divided by the original cross-sectional area. When the rate of increase in resistance to deformation per unit of actual area represented by curve *A* falls below a certain minimum, curve *B* begins to slope downwards as shown at *n*. This is the ultimate tensile strength of the copper in its primitive condition, i.e. the point at which the load divided by the original cross-sectional area reaches a maximum. Suppose, however, the curve *B* is determined as far as the point *m* and the cross-sectional area at that point is now used to obtain the stress, then clearly the remainder of the curve will follow the course indicated by *cde* on which *d* is the ultimate tensile stress. Similarly, if the curve *B* is determined as far as *h*, and the cross-sectional area at this point is now used to obtain the stress, then the remainder of the curve will follow the course *fg* on which *f* is the ultimate tensile stress. Finally, if the curve *B* is determined as far as *q* and the cross-sectional area at this point is now used to obtain the stress, then the remainder of the curve will follow the course *lk*.

If three test-pieces are stressed until the reductions in area represented by *m*, *h*, and *q* respectively are produced, and if these are now subjected to a test in which the stress calculated on the area at the

beginning of the second loading is plotted against reduction in area expressed as a percentage of the area at the beginning of the first loading, a series of curves like those shown in Fig. 65 will be obtained. The greater the extent to which the specimen is deformed prior to the test, the higher is the ultimate tensile strength. Point *s* (Fig. 64) indicates the breaking stress of the copper, and in a tensile test all specimens break when this particular stress is applied. The above discussion is concerned solely with the tensile test and the only variable considered is the area by which the load is divided to obtain the stress. If *x* is the breaking load, then *s* equals *x* divided by the actual area at the time of fracture, *k* equals *x* divided by the area at *g*, *g* equals *x* divided by the area at *h*, *e* equals *x* divided by the area at *m*, and *t* equals *x* divided by the original cross-sectional area. The breaking load does not alter, neither does the true breaking stress obtained by dividing by the actual area at the time of fracture, but the breaking stress obtained by dividing by any other area decreases as the area increases.

The operation of wire-drawing resembles the tensile test in that the cross-sectional area is decreased by mechanical deformation, and the ultimate tensile stress calculated on the reduced area is increased. In wire-drawing, however, the reduction in area is not brought about entirely by a tensile pull, but mainly by the circumferential pressure of the sides of the die. As shown by the above discussion of tensile deformation the ultimate tensile stress may be increased in this way until it equals the breaking stress, i.e. if a test-bar of copper in its primitive state is reduced in area by a tensile pull until its new area is that at *t* (Fig. 64), then on again loading and calculating the stress on the new area the ultimate tensile stress will be *s*. It is clear, however, that it is impossible in this way to raise the ultimate tensile stress above the breaking stress in the primitive condition, or to alter the breaking stress, for varying the method of calculating the stress has no effect on the metal. The question then arises whether it is possible by wire-drawing to increase the breaking stress.

A certain amount of experimental evidence has been obtained to show that the breaking stress is not altered by the wire-drawing operation. Thus, O'Neill (47) subjected steel to various amounts of reduction in area up to 78 per cent. by wire-drawing and tested it in tension after

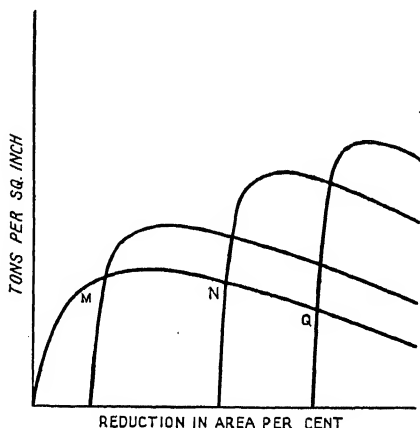


FIG. 65.

each reduction. He found that the true breaking stress was practically constant for material reduced different amounts by wire-drawing. Müller (48) obtained similar results for copper. Against these experiments may be set the following data: According to Jeffries and Archer (17) pure iron tested in tension in its primitive state has a breaking stress of 36 tons per sq. in. Yet it can be cold-drawn to give an ultimate tensile stress of 67 tons per sq. in. and a breaking stress of 74 tons per sq. in. Longmuir (49) drew iron wire until it gave an ultimate tensile stress of over 100 tons per sq. in. and the breaking stress would of course be higher than that. The steel used for making the wire for high strength wire ropes has a tensile stress of about 60 tons per sq. in. and a breaking stress of about 90 tons per sq. in. Yet for rope wire it is drawn until it has an ultimate tensile stress of 110 to 120 tons per sq. in., and for piano wire it is drawn to 180 tons per sq. in.

Increasing the tensile strength of metal by wire drawing depends on the same phenomenon as increasing its strength by stressing in tension, but owing to the different ways in which the deformation is produced in these two operations they are by no means strictly analogous. In general, the extent to which the tensile strength of a metal may be raised by wire-drawing is not restricted by the breaking stress of the metal as revealed in a tensile test. There must be some limit, however, to the extent to which the strength may be raised in this way. Under certain conditions it is reached when the capacity of the material for permanent deformation is exhausted, i.e. the stress required to produce further deformation is greater than the breaking stress. This occurs in the tensile test at the point of fracture, but in wire-drawing deformation may be continued beyond this so that a greater reduction in area is obtained and a higher breaking stress is reached. Under other conditions (e.g. in softer metals) the limit is reached when no further strain-hardening occurs. As already stated, the amount of strain-hardening produced by a given amount of deformation decreases as deformation proceeds, and in certain metals it ultimately becomes negligibly small. When this condition is reached, drawing may be continued without further increasing the resistance to deformation. The extent to which the strength may be increased by drawing is limited by the amount of strain-hardening, and the extent to which the metal may be reduced by drawing is limited by the fact that when the reduction in area approaches 100 per cent. no further reduction is possible.

TERMS USED IN DESCRIBING MECHANICAL PROPERTIES

The mechanical properties of metals are those which determine their response to applied force, and as the application of force results in deformation and fracture they are the properties that determine resistance to these. Fundamentally, the mechanical properties are those attributes on which the relations between stress, deformation, and fracture depend,

but in practice these are not considered and mechanical properties are assessed in terms of the behaviour observed under certain standard conditions. Thus, by subjecting a metal to a tensile test its yield-point, ultimate tensile strength, elongation, and reduction in area may be measured, and, similarly, by means of the other tests described in Part III, hardness, endurance, and resistance to impact or to prolonged loading may be determined. These measurements give a quantitative expression of a particular aspect of the behaviour of the metal when subjected to the action of force under certain specified conditions, but they are not measurements of its mechanical properties in the same way as determinations of density, specific heat, or electrical conductivity are measurements of its physical properties.

The tensile test was the first method of testing to be devised, and hardness, impact, endurance, and creep tests are more recent developments. Each new method of testing may be regarded as a means of obtaining additional information about the mechanical properties, but it is nearer the truth to regard it simply as an additional method of detecting differences between one metal and another. It is usual to describe the mechanical properties of a metal by giving a list of the results obtained in various kinds of tests, and to compare different metals in terms of them. It is not always convenient, however, to make a table of test results in order to describe the behaviour of a metal when subjected to stress, and, consequently, a number of generally descriptive terms such as strength, hardness, brittleness, toughness, and ductility are used. The purpose of this section is to explain the meaning of these terms and the relations between them.

In general, the strength of a metal means its ultimate tensile stress as determined in a tensile test, and does not refer to its breaking stress. The endurance (i.e. the resistance to repeated stress) is usually related in a fairly definite manner to ultimate tensile stress. As already explained the property of ductility is the property of undergoing permanent deformation accompanied by an increase in resistance to deformation. It is characteristic of iron, nickel, copper, aluminium, and their alloys at atmospheric temperature, and may therefore be regarded as characteristic of the common metals generally. Thus, when a metal undergoes permanent deformation at atmospheric temperature, the deformation is assumed to be ductile, and when ductility is used in the quantitative sense, it means capacity for undergoing permanent deformation before fracture.

Strength takes no account of deformation and ductility takes no account of strength, but brittleness and toughness in so far as they relate to behaviour in the tensile test are terms that take account of both. It has already been shown that metals that have a high resistance to deformation have a low resistance to fracture, i.e. in the tensile test the ultimate tensile stress is the same as the breaking stress and both are low. Such metals are described as brittle. When the resistance to

deformation is decreased, the breaking stress and tensile stress increase, i.e. the brittleness diminishes, and when it is sufficiently decreased, the ultimate tensile stress and breaking stress are separated and both are high. Such metals are described as tough. On further decrease in the resistance to deformation the ultimate tensile strength decreases, i.e. toughness diminishes and ductility increases. Thus a ductile metal is one that undergoes a substantial amount of permanent deformation before fracture, and as the ultimate tensile strength increases with resistance to deformation up to a point, high ductility is usually associated with moderate or low strength. A brittle metal is one that undergoes little or no permanent deformation before fracture, and as this is associated with a low resistance to fracture, brittleness is usually accompanied by moderate or low strength. A tough metal is one that undergoes sufficient permanent deformation to raise resistance to fracture to a maximum, and not enough to result in a lowering of the ultimate tensile stress by deformation. In such a metal high strength is associated with a moderate amount of deformation.

The relations between brittleness, toughness, and ductility are such that there is a gradual transition from one to the other and the lines of demarcation between them are not clearly defined. When a given specimen of a metal is subjected to a tensile test, it is usually easy enough to decide whether the results obtained indicate brittleness, toughness, or ductility. But unless the metal is definitely ductile or brittle, it cannot be concluded that it will always behave in the same way in a tensile test or that the test performed is a true indication of the way in which it will behave in other kinds of tests or in service. Variations in the conditions under which the tensile test is carried out will not cause a ductile metal to appear tough or a tough metal to appear ductile, but certain metals may appear either tough or brittle according to the degree of care taken to ensure axial loading, or the relations between the length and diameter of the specimen tested. In other types of tests, e.g. impact tests, and in service, metals that appear to be tough in the tensile test may be shown to be brittle. Thus the tensile test cannot be regarded as a completely reliable indicator of the nature of a metal. Fuller information may be obtained by performing impact tests in addition to tensile tests, but the true criterion is the behaviour of the metal in service. To ensure that toughness in the tensile test will not appear as brittleness in service, it is usual to sacrifice some strength in order to decrease the resistance to deformation to such an extent that any tendency to brittleness is eliminated.

The hardness of metals is measured by forcing a hard steel ball, a diamond cone, or a diamond pyramid into the metal under a specified pressure. The size of the impression thus produced is a measure of its hardness. The indentation hardness is a measure of resistance to deformation and is clearly related to the ultimate tensile stress of tough or ductile metals. It is not affected, however, by resistance to fracture,

so that brittle metals have a high hardness because of their high resistance to deformation. Indentation hardness does not necessarily indicate resistance to wear or to cutting.

The relations between the terms described above may be shown as follows:

Brittleness, associated with moderate or low strength and high hardness.

Toughness, associated with high strength and moderate hardness.

Ductility, associated with moderate or low strength and low hardness.

CHAPTER IV

TIME, TEMPERATURE, AND DEFORMATION

IN the previous chapter the mechanism and effects of deformation have been considered in relation to the applied stress, and it is now necessary to take account of the influence of time and temperature. These factors are of great importance in the treatment and use of metals, for the effects of mechanical shaping operations depend on the temperature at which they are performed, and metals may be subjected in use to prolonged loads either at atmospheric or elevated temperatures. The general relations between time, temperature, and deformation constitute the most complicated subject within the scope of this book. These relations vary from metal to metal. If the whole range of temperature between the melting-point of each metal and the lowest temperature at which it can be studied is considered, there is a marked similarity in the general relations between time, temperature, and deformation as displayed by the different metals. At any particular temperature, however, the effect of these factors varies from one metal to another. From this point of view the seven metals with which this work is mainly concerned may be arranged in the order iron, nickel, copper, aluminium, zinc, lead, and tin, and divided into three groups containing respectively iron and nickel, copper and aluminium, and zinc, lead and tin. Speaking generally, the effects of time and temperature may be considered to be similar in metals in the same group, and within limits alloys may be regarded as belonging to the same group as their basis metal. The behaviour of the metals iron and nickel at atmospheric temperature is the datum line from which the discussion of the relations between time, temperature, and deformation is approached. When these metals are heated the relations under consideration change, and at a sufficiently high temperature they resemble those observed in zinc, lead, and tin at atmospheric temperature. The results for iron and nickel at atmospheric temperature apply to some extent to copper and aluminium but not to zinc, lead, and tin; while those for iron and nickel at elevated temperatures apply to copper and aluminium at lower temperatures and to zinc, lead, and tin at atmospheric temperature.

In addition to complications arising from the varied behaviour of the different metals there are even greater ones associated with the relations between the factors under consideration. In the first place, account must be taken of the relations between deformation and time and between deformation and temperature. Then the general relations between the three may be considered. But a deformed metal is not stable, and after deformation it undergoes changes that are influenced by time and temperature which in turn affect the resistance to deformation. The relations between these changes on the one hand, and time, temperature,

and deformation on the other, must be considered, so that in the final analysis of any one metal at least four factors have to be dealt with, and as each of these reacts on the others, the complexity of the subject is evident.

Two major difficulties are encountered in considering the relations described above. One of them arises from the fact that in dealing with the effect of time on deformation the changes that follow deformations must intervene to a greater or less extent, and it is almost impossible to say whether a given phenomenon should be attributed to the relations between time and deformation or to those between time, deformation, and the changes that follow deformation. The other difficulty is also connected with the changes that succeed deformation. In general, deformation is followed by changes in the metal that result in an increase followed by a decrease in resistance to deformation. There is no doubt that the decrease in resistance to deformation is a fundamental feature of the relations between deformation, time, and temperature, but the same cannot be said about the increase. In many alloys an increase in resistance to deformation takes place with time even when they have not been deformed. This phenomenon is considered in Chapter VI. It depends on the 'precipitation' of some constituent from solid-solution in the basis metal of the alloys and is known as 'precipitation-hardening'. Now, although this phenomenon will occur in the absence of deformation, it is sometimes accelerated by it. Consequently, unless we are dealing with an absolutely pure metal in which no precipitation can occur, we cannot neglect the possibility of precipitation-hardening after deformation. The increase in resistance to deformation that follows deformation may be in every case the result of precipitation. Alternatively there may be an entirely distinct phenomenon that causes an increase in resistance to deformation in the absence of precipitation.

It has been shown that an increase in resistance to deformation may be caused by precipitation-hardening in a deformed metal, but it is difficult to show that such an increase can also occur when precipitation-hardening is impossible. Thus at the present time it is impossible to say whether or not two different phenomena are concerned. In any case their effects cannot be separated, and we may provisionally adopt the view that strain-ageing, as the phenomenon under consideration is called, is due to 'precipitation' while not ignoring the possibility that similar results may arise from a phenomenon that is a fundamental feature of the relations between deformation, time, and temperature.

DEFORMATION AND TIME

In order to avoid any confusion in the following discussion it is necessary to distinguish clearly between resistance to deformation per unit of actual area and resistance to deformation per unit of original area, which is of course proportional to the resistance to deformation of the

test-bar as a whole. The resistance to deformation per unit of actual area is the more fundamental quantity, for it is directly related to the amount of deformation. The resistance to deformation of the test-bar as a whole depends on the area as well as on the resistance to deformation per unit of actual area. Thus, when a bar is deformed by a tensile pull, the cross-sectional area decreases while the resistance to deformation per unit of actual area increases. So long as the rate of increase in resistance to deformation per unit of actual area is greater than the rate of decrease in area, the resistance to deformation of the bar as a whole increases. But when the rate of increase in resistance to deformation per unit of actual area becomes less than the rate of decrease in area the resistance to deformation of the bar as a whole decreases. Throughout the following discussion attention will be devoted mainly to the resistance to deformation of the bar as a whole.

If the yield-point phenomenon peculiar to iron and steel within a certain range of temperature is left out of account, it may be said that when a test-bar is continuously deformed, as in a tensile test, its resistance to deformation first increases and then decreases, thus giving rise to a maximum on the curve connecting load (or stress per unit of original area) and extension. Such a curve is shown in Fig. 27.

As the load on a test-bar is gradually increased from zero towards the maximum tensile stress, the resistance of the bar to deformation increases so as to balance the load, and consideration of the form of this part of the curve suggests that when a given load has been applied a further increase in load will be required to produce a further amount of deformation. Suppose now that the load is increased from zero to some value less than the ultimate tensile stress and is then maintained constant. When it attains the value at which it is to be maintained constant, it is balanced by the resistance to deformation of the test-bar, and what takes place under the constant load depends on the combined effect of load and time on the resistance of the bar to deformation.

It is evident that when a constant load is applied to a bar, the resistance to deformation may either remain constant, or increase or decrease with time, and according to the metal, the magnitude of the load, and the time and temperature of its application, any of these conditions may actually be realized. For the present, however, attention will be confined to a study of what happens when iron, nickel, copper, aluminium, or their alloys are subjected at atmospheric temperature to a load that is less than the maximum tensile stress. In this case the resistance to deformation increases with time.

Conditions Realized when Resistance to Deformation increases with Time.

When a gradually applied load attains the magnitude at which it is to be maintained constant, it is balanced by the resistance to deformation of the test-bar. If this resistance now proceeds to increase with

time under constant load, it might be expected that the bar would completely resist further deformation under that load. Actually, however, deformation proceeds, and the capacity to deform under a constant load while resistance to deformation is increasing is an important feature of the relations between time and deformation. This seems like a contradiction in terms, for the fact that the deformation continues would appear to show that the resistance to deformation is not increasing. Nevertheless, it is an established characteristic of the deformation of metals, and it is now proposed to consider progressive deformation while the resistance to deformation is (a) increasing and (b) decreasing.

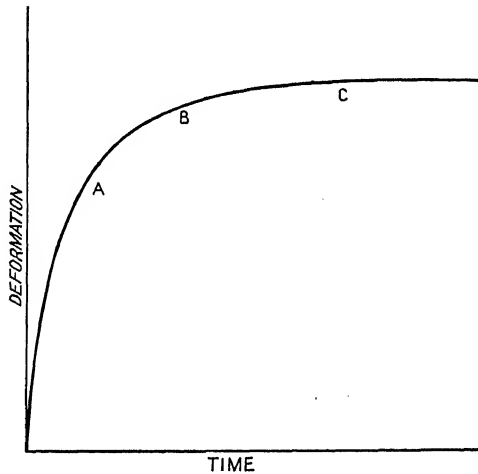


FIG. 66. Deformation-time curve. Resistance increasing.

When a metal is subjected to a constant load under such conditions that its resistance to deformation increases with time, the curve connecting time and deformation is of the form shown in Fig. 66. The amount of deformation taking place in successive equal time intervals decreases as the total time under load increases, and as the amount of deformation becomes very small, it eventually appears to stop at a point that depends on the sensitivity of the apparatus used to measure it. The respective scales for the ordinate and abscissa in Fig. 66 depend on the metal, the temperature, and the magnitude of the applied load. At low loads a very small amount of deformation takes place in a very long time, but as the load is increased towards the ultimate tensile stress progressively larger amounts of deformation take place. Increasing the temperature has a similar effect to increasing the load, while if the metals iron, nickel, copper, aluminium, zinc, lead, and tin are subjected at the same temperature to loads that are equal fractions of their ultimate tensile strength, the amount of deformation taking place in a given time increases from metal to metal in the order given.

The relations between time and deformation indicated in Fig. 66

determine the behaviour of metals when subjected to (1) loads that are progressively increased at different rates, (2) single constant loads applied for long periods, and (3) loads that are increased in steps. The third method of loading shows very clearly that the resistance to deformation increases with time under constant load and may be considered first.

The curves shown in Fig. 67 were determined by Hanson and Wheeler (23) and show the behaviour of aluminium test-bars when subjected to loads that were increased in steps and maintained constant at each step until no further deformation could be measured by the extensometer, which could be read to 0.001 in. The figures on the curves give the time in days represented by the various portions, and the complete tests occupied 234 days for the single crystal and 575 days for the polycrystal aluminium. Curve 2 for polycrystal aluminium does not show the relations between time and deformation, but simply indicates by its horizontal portions the total amount of extension that took place while the load was maintained constant at different values. Actually, if the conditions represented by this curve are considered as a whole, they are seen to be very complicated. Had a different specimen been used to study the effect of each load the amount of deformation that took place before the rate of deformation became too small to measure would have been observed to increase regularly with the load. Under the conditions realized, however, the behaviour of the specimen under each load is influenced by the effect of the previously applied loads. For the present purpose, however, the important feature of the curve is that it consists essentially of horizontal and vertical portions. The horizontal portions show the amount of extension that took place at a decreasing rate under constant load during the time shown. The vertical portions show that after deformation with time under constant load further deformation does not begin whenever the load is increased. To obtain this it must be substantially increased, which proves that the resistance to deformation increases with time under constant load just as it does under a progressively increasing load.

The effect of single constant loads applied for long periods is evident from what has been said above. If extension is plotted against time, a curve like that shown in Fig. 66 is obtained for each load, but the scales on the ordinate and abscissa vary with the load so that the time required to produce a given amount of deformation decreases while the total amount of deformation produced increases with the load. If the load is plotted against extension, a horizontal line like that shown in Fig. 67 is obtained for each load and the lines become longer as the load becomes greater. The effect of loads that are progressively increased at different rates may next be considered. For every load, as explained above, there is a time-deformation curve like that shown in Fig. 66, and the curves for all loads between zero and the ultimate tensile stress form a surface which shows the relations between load, time, and deformation. Every

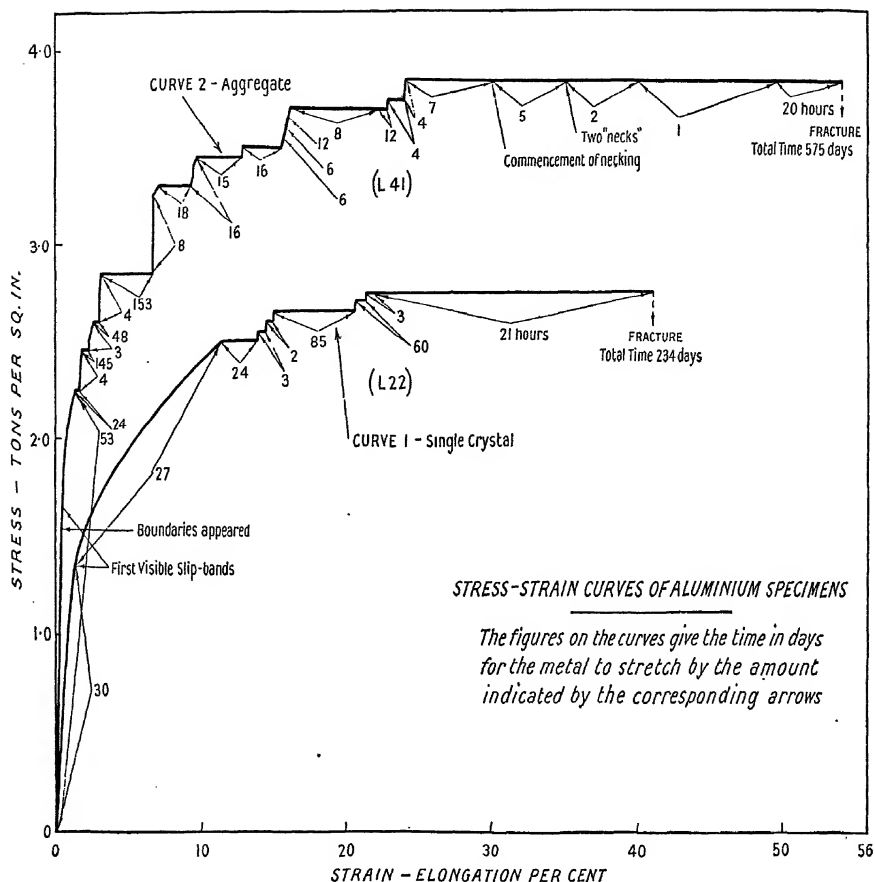


FIG. 67. Slow-loading curves—room temperature. (*Journal of the Institute of Metals.*)

curve obtained by increasing the load at a certain rate and plotting load against extension lies on this surface. The more rapid the rate of loading the shorter is the time interval during which each increment of load acts, and the smaller is the amount of deformation produced by it. Thus the load-extension curve must become steeper as the rate of loading is increased, but the effect of variation in the rate of loading varies considerably in different ranges. Thus with a given rate of loading the deformation corresponding to each increment of load may be that indicated by a point such as *B* (Fig. 66) on the time-deformation curve concerned. If the rate of loading is decreased, the deformation corresponding to each increment of load may be that indicated by a point such as *C* (Fig. 66), and the form of the stress-strain curve will not be greatly affected. If, however, the rate of loading is increased so that the deformation corresponding to each increment of load is that indicated by a point such as *A*, then there will be a pronounced increase in the steepness of the stress-strain curve. In order to achieve this last effect very rapid loading is required.

In order to simplify discussion of the complicated phenomena with which which this chapter is concerned the changes that follow deformation are not being considered in the meantime, and we are endeavouring to explain the relations between time and deformation without regard to the effect of these changes on resistance to deformation. We have just seen that deformation can proceed with time although the resistance to deformation is increasing. If this resistance were not increasing, the rate of deformation would not decrease with time, and it would not require a substantial increase in load to produce further deformation after a certain load had been applied for a long time. The question may be asked whether a given amount of deformation produced by the prolonged application of a constant load has the same effect on the resistance to deformation as an equivalent amount of deformation produced by an increasing load? This is a question that cannot be answered, for both load and time must always be considered, and we have no method of measuring resistance to deformation except in terms of load and time. It is evident that the extent to which a metal must be deformed in order to sustain a given load increases with the time for which the load is applied. If a given load is applied for an infinitely short time, it produces no deformation at all. If it is applied for 1 second, it produces let us say an extension of 1 per cent., if applied for 1 minute, an extension of 2 per cent. The longer the period of application of the load the greater is the amount of deformation produced by it, and the greater is the extent to which the metal is strain-hardened. In the case mentioned above we know that after 2 minutes' application of the load the metal has been strain-hardened sufficiently to sustain this load after 2 minutes. To sustain it after 2 hours it will need to be further strain-hardened. If instead of maintaining the load constant for more than 2 minutes we start to increase it, we may hope to find what increase in load is equiva-

lent to 2 minutes' application of the lower load in terms of strain-hardening. We must, however, increase the load at some particular rate. Suppose we increase it rapidly and find that no deformation takes place until it has been increased by 100 lb. we cannot say that 2 minutes under load X lb. has the same strain-hardening effect as $X+100$ lb. All we know is that 2 minutes under load X has the same strain-hardening effect as an additional load of 100 lb. applied rapidly. If we increase the load slowly, further complications are introduced, for with each small addition of load the influence of both load and time comes into play, and the point at which we observe further deformation to begin under the increasing load depends on the magnitude of the load increments, the time intervals at which they are added, and the sensitivity of the extensometer.

The effect of the changes that follow deformation will have to be considered before it is possible to deal with the results actually obtained when metals are loaded at different rates or subjected to the prolonged action of constant loads of different magnitude. Some aspects of the effect of time on mechanical properties may, however, be considered now. The ultimate tensile stress is reached when

the slope of the curve connecting deformation and resistance to deformation per unit of actual area falls below a certain value (see A , Fig. 29). When we apply a progressively increasing load at a certain rate, the ultimate tensile stress is reached after a certain amount of elongation. The question now arises as to how the ultimate tensile stress and uniform elongation are affected by the rate of loading. If, e.g., curve E (Fig. 68) is obtained by loading at a certain rate up to the ultimate tensile stress, will curve F , obtained with a more rapid rate of loading up to the ultimate tensile stress, stop at a , continue to b , stop at some point intermediate between a and b , or continue beyond b ? In other words, will the ultimate stress a , or the uniform elongation b , be independent of the rate of loading, or will both be altered? Clearly the answer depends on how the curve A (Fig. 29) is affected by time. If the point d (Fig. 29) is reached after a certain amount of deformation irrespective of variations in the relative effects of time and stress in producing this deformation, then curve F (Fig. 68) obtained with more rapid loading will continue to b . If, however, the point d is reached at a certain stress, then curve F will stop at a . The former alternative is the more probable and something approximating

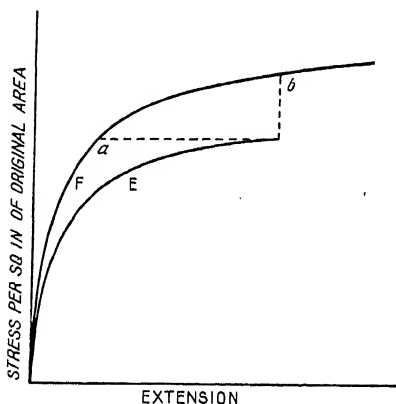


FIG. 68. Stress-strain curves for different rates of loading.

to this may be expected to occur. At the same time, this condition is not likely to be exactly realized for it would mean that the form of curve *A* (Fig. 29) is unaffected by time. Thus, although we can conclude that the ultimate tensile stress will increase with the rate of loading and that the uniform elongation will probably be altered, we cannot say definitely whether the alteration will involve an increase or a decrease.

Conditions Realized when Resistance to Deformation decreases with Time.

As already explained the resistance to deformation at present under discussion is that of the test-bar as a whole, and this is proportional to

the resistance to deformation per unit of original area. As the resistance to deformation of the test-bar as a whole is equal at all times to the resistance to deformation per unit of actual area multiplied by the actual area, it is affected both by strain-hardening and by reduction in area. During tensile deformation the resistance to deformation per unit of actual area increases while the actual area decreases. In the early stages a given reduction in area is accompanied by a large increase in resistance to deformation per unit of actual area and the resistance of the bar as a whole increases.

But the amount by which the resistance to deformation per unit of actual area is increased by a given reduction in area diminishes as deformation proceeds and eventually becomes so small that the resistance of the bar as a whole decreases. Thus the curve connecting reduction in area and resistance to deformation per unit area has the form represented by *A* (Fig. 69), while the curve connecting reduction in area and resistance to deformation of the bar as a whole has the form represented by *B* (Fig. 69).

Curves *A* and *B* (Fig. 69) are the same as the corresponding curves in Fig. 29. *e* on curve *B* is the maximum tensile stress, and when a specimen is deformed to this point, its resistance to deformation begins to decrease. Thus, if a load equal to the ultimate tensile stress is applied and maintained, the metal will continue to deform at an increasing rate until fracture occurs. Deformation under a constant load may proceed while the resistance to deformation is increasing or while it is decreasing, but the two cases are distinguished by the fact that in the former the rate of deformation diminishes with time while in the latter it increases.

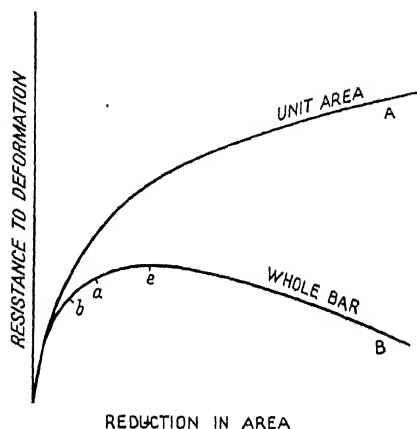
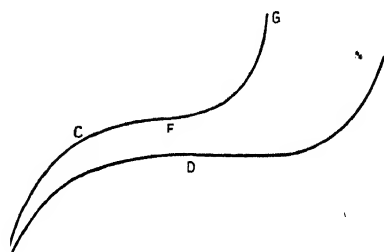


FIG. 69. Resistance to deformation
A unit area, *B* total area.

There is nothing remarkable about a specimen extending to fracture under a load equal to its maximum tensile stress. What is significant, however, is that it can in time extend to fracture under a load less than its ultimate tensile stress. This is, in a sense, another contradictory expression, but there is no such thing as an ultimate tensile stress that is independent of time, and the correct way of stating the case under consideration is to say that the ultimate tensile stress depends on stress and time and occurs at a lower stress after a longer time. To avoid confusion the point *e* in Fig. 69 will be referred to as the point of maximum resistance to deformation.

If a test-bar is loaded in tension until it is reduced in area to the point *a* (Fig. 69), and the load is then maintained constant, the specimen will continue to deform under this load although the resistance of the bar is increasing. Thus, while the load is maintained constant the portion *ae* of curve *B* may be traced in time. During this time the cross-sectional area is decreasing, but the resistance of the bar to deformation is increasing and each successive equal increment of deformation requires a longer time. If the relations between time and deformation are plotted, the portion *OF* of curve *C* (Fig. 70) is obtained. When the point *e* on curve *B* (Fig. 69) is reached as a result of the prolonged action of the constant load, the test-piece attains its maximum resistance to deformation. Thereafter it begins to decrease as deformation proceeds, and consequently the rate of reduction of area begins to increase. Thus, if the relations between time and deformation during this stage are plotted, the portion *FG* of curve *C* (Fig. 70) is obtained. The area decreases at an increasing rate until fracture occurs. If, now, a similar test-bar is loaded in tension until it is reduced in area to the point *b* (Fig. 69) and the load is then maintained constant, the same phenomenon will be observed, but the time that will elapse before the specimen reaches its maximum resistance to deformation will be much longer as shown by curve *D* (Fig. 70).



TIME

FIG. 70. Deformation-time curves showing creep at a diminishing rate to a minimum followed by creep at an increasing rate to fracture.

Continuous deformation under constant load is known as 'creep' and is a most important phenomenon from a practical point of view. Further attention will be given to it in a later section and also in Part III. Meanwhile it may be said that it proceeds at a decreasing rate when the resistance of the bar to deformation is increasing and at an increasing rate when the resistance of the bar to deformation is decreasing. As continuous tensile deformation of a bar is accompanied first by an increase,

succeeded by a decrease, in resistance to deformation, and as these two different phases are parts of a continuous phenomenon, it follows that creep at a decreasing rate will eventually become creep at an increasing rate. At the point of inflexion it will proceed at a constant rate, and this represents the temporary condition in which the resistance to deformation remains constant under a constant load. Curve *C'* (Fig. 70) is a general creep curve showing deformation against time, but according to the metal, the load, and the temperature, the point *F* may be reached after minutes, days, months, years, or an infinite time. The explanation of creep in terms of crystal structure is linked up with the explanation of several other aspects of the response of metals to applied force. Thus, although we know that a metal can deform at a decreasing rate under constant load while its resistance to deformation is increasing, we do not know why this occurs and we cannot expect to explain it while we are still in doubt as to the cause of strain-hardening.

DEFORMATION, TIME, AND TEMPERATURE

The elastic limit depends on the initial resistance to deformation, and the yield-point in iron and steel has a substantially similar meaning. The remainder of the stress-strain curve depends on the rate of strain-hardening, i.e. if this rate is high, the curve is steep, whereas if it is low, the curve is flat. In general the elastic limit and yield-point decrease with rising temperature. At sufficiently low temperatures an elastic limit is usually found, but at temperatures near the melting-points of the metals permanent deformation begins whenever a load is applied. Furthermore, at temperatures near their melting-points metals do not strain-harden and the rate of strain-hardening increases as the temperature falls. Thus, if a given metal is tested, the elastic limit, yield-point, ultimate tensile stress, and uniform extension decrease, while the local extension and reduction in area increase with rising temperature.

Owing to the fact that an increase in temperature is accompanied by a decrease in the amount of strain-hardening produced by a given amount of deformation, the effect of time becomes more pronounced as the temperature of testing is raised. Thus, if the same stress is applied to a metal at two different temperatures, the time-deformation curve at the higher temperature will show more rapid deformation in the early stages and a slower decrease in the rate of deformation. Curves *C* and *D* (Fig. 70), which were drawn to illustrate the effect of different loads at the same temperatures, may also be taken to represent the effect of the same load at two different, but not widely separated, temperatures.

When iron and steel are subjected to a short-time tensile test at atmospheric temperature, each increment of load deforms the metal to an extent that may be supposed to be represented by point *B* on the time-deformation curve (Fig. 66). By substantially increasing the rate of loading a marked increase in the steepness of the curve may be obtained,

but a decrease in the rate of loading or the application of constant loads for long periods does not have a very pronounced effect. Some idea of the effect of variations in the rate of loading of mild steel may be obtained from the following results obtained by Quinney (50):

<i>Duration of Test</i>	<i>Yield-point</i>	<i>Tensile stress</i>
135 hrs.	12.25 tons/sq. in.	23.1 tons/sq. in.
2 min.	15.70	24.1
5 sec.	18.25	27.0

The total elongation increased as the rate of loading decreased. The effect of prolonged constant loads is not pronounced unless they are very near to the ultimate tensile stress as determined in the short-time test. This holds for nickel, and also for copper and aluminium. In zinc, lead, and tin, however, the effect of time is very pronounced even at atmospheric temperature.

Up to 350° C. the behaviour of iron and steel is influenced to a marked extent by the changes that follow deformation, but above this temperature deformation with time begins to become very important in those iron alloys that are not specifically intended to resist deformation at elevated temperatures. As the temperature is raised the effect of time becomes increasingly pronounced, and iron will creep to fracture under loads substantially less than the ultimate tensile stress determined in a short-time test. Nickel behaves in a similar way, but in the case of copper and aluminium the effect of time becomes of progressively increasing importance as the temperature is raised above that of the atmosphere. At 350° C. these metals and most of their alloys will creep to fracture under quite low loads, and as a result they are unsuitable for use at temperatures above this. Zinc, lead, and tin are very susceptible to the effect of time at atmospheric temperature, and as this effect increases rapidly with rising temperature, they are not suitable for use at temperatures above those of the atmosphere.

CHANGES THAT FOLLOW DEFORMATION

As a result of the various changes that occur during deformation an unstable condition of the crystal structure is produced. Instability implies a tendency to change, and deformation thus initiates a series of changes which under the appropriate conditions eventually lead to the replacement of the original deformed crystals by a new system of crystals which grow out of them. Some aspects of these changes are well understood while others are not, but consideration of their mechanism may be deferred for the time being and attention confined to their effects and the conditions under which they proceed.

In general the changes that follow deformation result in an increase followed by a decrease in resistance to it. The rate at which they proceed and the magnitude of their effects depend on the nature of the metal, the amount and temperature of deformation, and the temperature at which the metal is subsequently maintained. The effects of these

changes are most conveniently observed when a metal is deformed under such conditions of time, temperature, and deformation that no change takes place during distortion. In this case the increase and decrease in resistance to it that follow may be separately studied. It is doubtful whether such conditions can ever be realized completely, but they are very closely approached when iron or nickel is deformed fairly rapidly at atmospheric temperature. When the above conditions are not obtained, the changes that follow the first stages in deformation affect the behaviour of the metal during the subsequent stages, and the nature of their effect depends on the relation between the rate of deformation and the rate of the changes. If the rates are so adjusted that the hardening effect of the changes comes into operation, then the result is an increase in resistance to deformation, while if the softening effect becomes operative, then the result is a decrease in resistance to deformation.

When iron or steel is deformed fairly rapidly at atmospheric temperature, as in a tensile test or a cold-working operation, the changes that follow do not proceed to any appreciable extent during the deformation itself. If the metal is retained at this temperature, the changes proceed slowly and an increase in resistance to deformation occurs. At atmospheric temperature they do not reach the stage at which a decrease in resistance to deformation begins, so that iron and steel after distortion become harder with time. This phenomenon is known as strain- or mechanical-ageing. If the metal is heated after deformation, the rate of the changes is accelerated and what takes place in months at atmospheric temperature may be produced in minutes by heating. Ageing is an unsuitable term to apply to a change that takes place in a few minutes, but in order to avoid introducing a new one it will be used generally to denote that phase of the changes following deformation in which an increase in hardness takes place. If the temperature of heating is sufficiently high or the time sufficiently long, the changes that follow deformation reach a stage at which the metal begins to soften. Under certain conditions this coincides with the beginning of recrystallization, i.e. the replacement of the original deformed crystals by a new set. Under other conditions softening sets in first. Nevertheless it is customary to attribute the softening to recrystallization and, except where it is necessary to distinguish them, recrystallization will be used to denote that phase of the changes following deformation in which a decrease in hardness takes place.

The general relations between deformation, time, and temperature must now be considered, taking account of the changes that follow deformation and the differing behaviour of different metals. This can be most conveniently and clearly accomplished by dealing with typical cases illustrating (1) the effect of the rate of loading at atmospheric temperature, (2) the effect of time at atmospheric temperature, (3) deformation at atmospheric temperature followed by heating, and (4) deformation at elevated temperatures.

EFFECT OF RATE OF LOADING AT AIR TEMPERATURE

Iron and steel may be considered first. It has already been explained that when the changes that follow deformation are left out of account the stress-strain curve tends to become steeper as the rate of loading is increased. This is due to the fact that the amount of deformation produced by a given load increases with the time for which the load is applied, and consequently, the ultimate tensile stress tends to decrease with decrease in the rate of loading. The changes that follow deformation produce in the first instance an increase in resistance to it, and in iron and steel at atmospheric temperature this stage is never passed. We may suppose continuous loading to take place in a series of steps. In each step a certain amount of deformation is produced, and following this the resistance to it increases with time. When the next increment of stress is applied the amount of deformation produced by it decreases as the time that has elapsed since the previous increment increases. Thus, when the changes that follow deformation come into operation, the stress-strain curve tends to become steeper as the rate of loading decreases, i.e. the ultimate tensile stress tends to rise as the rate of loading decreases.

It follows from the above that a decrease in the rate of loading may be accompanied either by a decrease or an increase in the steepness of the stress-strain curve and in the magnitude of the ultimate tensile stress. The observed result depends on whether we are dealing with the simple relations between time and deformation or with the additional influence of the changes that follow deformation. If the range of rates studied is confined to comparatively rapid loading the change that follows deformation does not have a marked effect and the tensile strength decreases with the rate of loading. When the rate of loading becomes slower the effect of strain-ageing becomes greater and the tensile stress tends to increase with decrease in the rate of loading. Whether this increase will be observed or not depends on the conditions of the test and the sample of metal studied. The relations between deformation, time, and strain-ageing are very complicated, for whereas strain-ageing proceeds with time its rate depends on the amount of previous deformation. Thus the magnitude of the steps by which the load is increased and the period of time between each step are important. Furthermore, the composition and heat-treatment of a particular sample of iron and steel have a marked influence on the rate and magnitude of strain-ageing as will be explained presently. Consequently, it is difficult to say whether a decrease in the rate of loading will, in a given case, cause an increase or a decrease in the ultimate tensile-stress. All that can be said is that either may be expected to occur, and that if similar specimens are studied over a wide range of rates of loading (i.e. from very fast to very slow) a minimum tensile strength should be observed at some intermediate rate.

In 1905 Hopkinson (51) showed that if a load exceeding that required to break a copper wire in a tensile test was applied for $1/1,000$ second the wire was not appreciably extended. This indicates that if the duration of application is sufficiently short a metal is not greatly affected by a load capable of breaking it. Similar results have since been obtained in endurance tests. These tests are fully described in Part III. The specimens studied in these cases are subjected to repeated cycles of stress which generally vary from a certain value in tension to a similar value in compression. If the range of stress exceeds a particular magnitude, the metal will fail after a certain number of cycles, and this number decreases as the range of stress increases. If, however, the range of stress

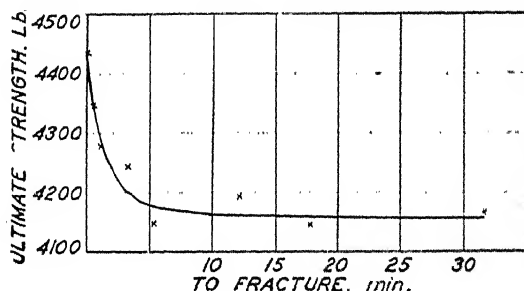


FIG. 71. Effect of rate of loading on tensile strength of steel wire.
(*Journal of the Iron and Steel Institute.*)

is less than this magnitude, the specimen will withstand an infinite number of cycles without failing. The maximum range of stress that can be safely applied an infinite number of times is known as the endurance range. If the frequency of the cycles is less than about 6,000 per minute, the endurance range is not appreciably affected by it; but as the frequency is raised beyond this, the endurance range begins to increase. The results actually obtained are considered on p. 473. Krouse (52) found that the endurance range of a number of materials increased by 2,000 to 12,000 lb. per sq. in. when the frequency of the stress cycles was increased from 10,000 to 30,000 per minute.

The above results show that the effect of a given stress decreases with the time for which it is applied. It follows from this that the tensile stress should decrease with the rate of loading. Quinney's results (already quoted) illustrate this and a more extensive study of the effect of rapid loading has been carried out by Ginns (53). This investigator subjected a number of materials to rapid tensile tests in which fracture was produced in about 0.005 seconds and compared the results with those obtained in tests of 2 minutes duration, which is of the same order as the time normally occupied by a tensile test. Some of the results obtained are shown below.

It will be seen from the above results that in every case the tensile stress is increased by increasing the rate of loading and sometimes, as

in the 0.15 and 0.48 per cent. C. steels, by a substantial amount. With the exception of copper and the 0.89 per cent. C. steel the elongation was decreased by increasing the rate of loading, and in most cases the reduction in area was also decreased. As already pointed out, it is uncertain whether the uniform extension should be increased or decreased by increasing the rate of loading, but it is very probable that the breaking stress will decrease and this should have the effect of decreasing the reduction in area and the local extension and hence the total extension.

<i>Metal</i>	<i>Speed of test</i>	<i>Tensile strength Tons per sq. in.</i>	<i>Elongation %</i>	<i>Reduction in area %</i>
Steel 0.15% C. . . .	Rapid	37.0	34.5	65.2
	Slow	29.1	39.5	71.0
Steel 0.34% C. . . .	Rapid	37.0	24.5	55.1
	Slow	34.5	30.0	58.0
Steel 0.48% C. . . .	Rapid	55.0	21.0	32.2
	Slow	43.2	24.0	45.0
Steel 0.75% C. . . .	Rapid	55.0	12.0	21.7
	Slow	54.0	14.0	20.0
Steel 0.89% C. . . .	Rapid	72.0	11.6	11.2
	Slow	65.2	9.4	10.5
Copper	Rapid	19.0	59.3	74.5
	Slow	13.8	54.0	76.0
Brass 30% C.	Rapid	24.0	65.3	74.4
	Slow	22.1	78.0	75.0
Brass 40% C.	Rapid	28.0	43.1	61.8
	Slow	26.4	47.0	62.0
Duralumin	Rapid	30.0	20.0	40.7
	Slow	27.0	24.0	35.0

A very effective illustration of the lowering of the tensile strength with decrease in the rate of loading is furnished by Fig. 71 taken from the 3rd Report of the Corrosion Committee of the Iron and Steel Institute.

In contrast to the above results which demonstrate that the effect of a given stress decreases with the time for which it is applied, and that the tensile strength increases with the rate of loading, several investigators have shown that the tensile strength may also increase with a decrease in the rate of loading. Thus Quinney (50) obtained the following results with wrought iron.

<i>Duration of test</i>	<i>Yield-point</i>	<i>Tensile stress</i>
2 min.	13.25 tons/sq. in.	18.75 tons/sq. in.
75 hrs.	9.9 " "	20.6 " "

It will be noted that in the longer test the stress at the yield-point decreases while the tensile stress increases. This is because the yield-point in iron and steel represents the beginning of deformation. Consequently, it is not affected by the changes that follow, but depends directly on the relations between deformation and time. Bottomley (54) found that the average tensile strength of some soft iron wires broken

in 10 minutes was 45.2 lb. One specimen was loaded with 43 lb. for 24 hours and then broken by a gradual increase of load during 25 minutes. It broke at 49.25 lb. Another specimen loaded for three days with 43 lb. subsequently broke at 51.5 lb. and a further sample broken by a gradual addition of load over two months broke at 57.25 lb. Further results obtained by varying the rate of loading at different temperatures will be referred to presently.

The general shape of the curve connecting ultimate tensile stress and rate of loading is shown in Fig. 72, and it is theoretically possible to determine a curve of this type for each metal at each temperature. The portion *ABC* depends on the fact that the amount of deformation pro-

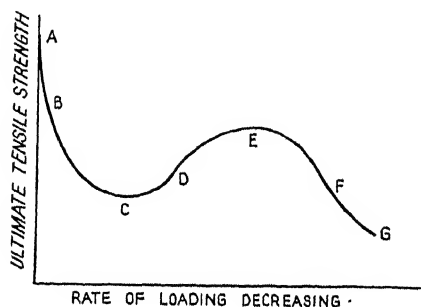


FIG. 72. Ultimate tensile stress vs. rate of loading.

duced by a given stress varies with the time for which it is applied. The portion *CDE* is determined by the fact that strain-ageing increases the resistance to deformation, and the portion *DEFG* by the fact that recrystallization decreases the resistance to deformation. So far as iron and steel are concerned it is in practice only possible to determine at atmospheric temperature the portion of the curve between *B* and *D*.

That between *A* and *B* cannot be readily determined because of the difficulty of measuring the tensile strength with very rapid loading, and that between *D* and *G* cannot be ascertained because of the slow rates of strain-ageing and recrystallization. Lowering the temperature would make it easier to determine the portion between *A* and *B*, while raising the temperature would make it easier to ascertain the portion between *D* and *G*.

In non-ferrous metals the bulge *CDEFG* on the curve is very slight, i.e. strain-ageing is not nearly so pronounced as in steel. Furthermore, in zinc, lead, and tin the recrystallization change proceeds quite rapidly at atmospheric temperature. In all the non-ferrous metals, therefore, (with the possible exception of nickel) the curve connecting tensile strength and rate of loading may be said to show a progressive decrease in strength with a decrease in rate of loading. Haigh and Jones (55) obtained the following results on lead specimens 8 in. in length between gauge marks and strained at different rates:

<i>Rate of straining</i>	<i>Ultimate tensile</i>
2 in. extension per min. (quick)	2,442 lb. per sq. in.
$\frac{1}{2}$ in. extension per min. (slow)	1,839 " "
2 in. extension per min. (quick)	2,405 " "
$\frac{1}{2}$ in. extension per min. (slow)	1,635 " "

Results obtained by Sachs in an investigation of the effect of the rate

of loading on copper and zinc are shown in Fig. 572, p. 1428. From this figure the following results are taken.

Metal	Duration of test	Ultimate tensile stress
Zinc	0.05 min.	20.0 Kg. per sq. mm.
"	500.00 "	13.5 " "
Copper	0.05 "	38.0 " "
	500.00 "	34.0 " "

Although strain-ageing is not pronounced in non-ferrous metals, and does not produce conditions under which the tensile strength increases with decrease in the rate of loading, it is nevertheless sufficiently marked to be detected under certain conditions. Several examples are given in

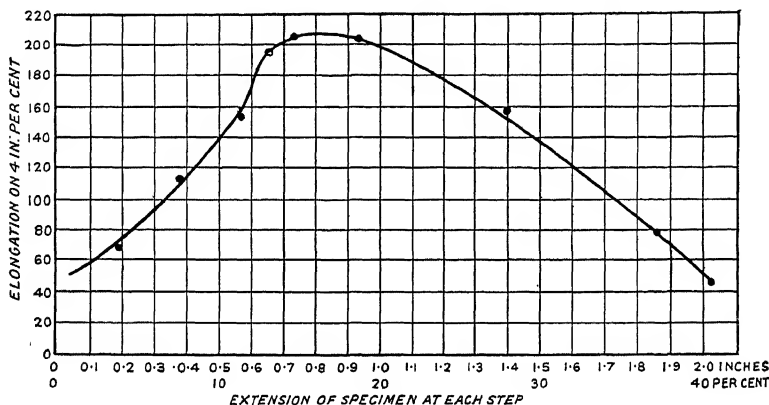


FIG. 73. Intermittent loading of lead. (*Journal of the Institute of Metals.*)

the following sections. In the meantime one striking case may be considered. The uniform elongation of a test-bar depends, like the ultimate tensile stress, on the extent to which deformation proceeds before the rate of strain-hardening becomes less than the rate of reduction in area, i.e. it depends on the position of the point *d* on curve *A* (Fig. 29). If a load is applied in steps with a time interval between each, then the amount of uniform extension will depend on whether strain-ageing or recrystallization takes place during the interval between each increment of load. If the former, the amount of uniform extension should increase; if the latter it should decrease. Thus the amount of uniform extension varies with the metal, the load-increments, and the time intervals.

When lead is subjected to a tensile test under ordinary conditions, most of the extension is local as shown by the following results obtained by Haigh and Jones:

Elongation on 2 in.	118 per cent.
" " 8 in.	53 " "

By increasing the load in steps, and adjusting their magnitude and the intervals between them to obtain the maximum effect of strain-ageing,

much of the local can be converted into uniform extension. This has been demonstrated by Chaston (56) who studied the effect of different strain-increments and rest periods. The curve connecting strain-increment and total elongation for constant rest periods of 5 minutes is shown in Fig. 73. The total elongation first increases with an increase in the amount of deformation at each step. This is due to the fact that the amount of strain-ageing during each 5 minutes rest period increases with the amount of deformation per step. When the amount of strain per step is increased above an extension of 0.8 in. the total elongation begins to decrease with an increase in the strain-increments. This is due to the fact that with the larger strain-increments the changes that follow deformation proceed beyond the strain-ageing stage and enter the recrystallization stage during the five minutes rest periods.

THE EFFECT OF TIME AT ATMOSPHERIC TEMPERATURE

It is evident from what has been said in the previous section that the resistance of iron and steel to deformation should increase with time after deformation. This aspect has been the subject of many investigations and is more fully considered in Chapter XII. Fig. 74, determined by Hudson (57), illustrates this change, and shows the percentage increase with time of the load required to break $3\frac{1}{2}$ S.W.G. wires of mild steel previously cold-worked by a 24 per cent. reduction in area in a wire-drawing die. Table 17, determined by Pfeil (58), shows the increase in tensile stress with time of a steel wire previously reduced in area 22.8 per cent. by wire-drawing.

TABLE 17

Strain-ageing of 0.11 per cent. Carbon Steel Wire

<i>Time after drawing</i>	<i>Tensile strength tons per sq. in.</i>	<i>Increase in strength tons per sq. in.</i>
0	30.9	..
10 min.	31.0	0.1
70 "	30.8	..
170 "	30.9	..
6 hrs.	31.0	0.1
23 "	31.15	0.25
5 days	31.6	0.7
12 "	32.1	1.2
29 "	32.6	1.7
43 "	33.0	2.1
119 "	33.1	2.2

Some slight increases in the hardness of deformed non-ferrous metals have been observed to occur with time at atmospheric temperature but in general decreases in hardness result.

Closely related to strain-ageing is the phenomenon of overstrain and recovery. It was shown in Chapter III that the high elastic limit and sudden yield of iron and steel are not exhibited by single crystals,

and become more and more pronounced as the number of crystals in a given volume increases. The initial resistance to deformation of these metals therefore depends on the mutual interference of the crystals. When a specimen is stressed above its yield-point, this interference is overcome, and if it is unloaded and then reloaded the conditions realized are different from those which existed during the original loading.

It has already been explained that most of the deformation which a given load can produce takes place during the first application. Nevertheless, on unloading and reloading, a further but substantially smaller

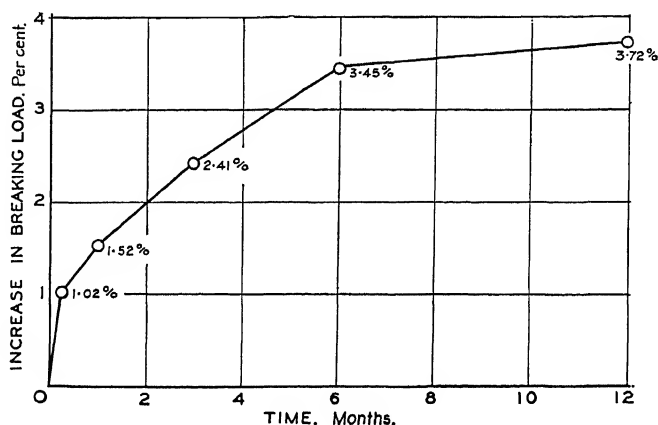


FIG. 74. Strain-ageing of mild steel. (*Journal of the Iron and Steel Insti*

amount of distortion is produced by the same load, and this continues during many stress-cycles. In the particular case of iron and steel this capacity for deforming progressively when loaded up to the same point, combined with the breakdown of the initial resistance to deformation caused by stressing beyond the yield-point, gives rise to the phenomenon known as overstrain which may be explained as follows: During the initial loading no permanent deformation occurs below the elastic limit and little occurs below the yield-point. At this point, however, a substantial amount takes place as a result of the breakdown of the initial resistance to deformation, caused by the mutual interference of the crystals. If, after the yield-point has been exceeded, the load is taken off and reapplied immediately, the amount of deformation that occurs during loading up to the same point is substantially less than before. But the high initial resistance to deformation does not require to be overcome, and a smaller amount of deformation takes place progressively as the load is increased instead of taking place suddenly when a certain stress is exceeded. Thus during the second loading measurable amounts of permanent deformation occur at a much lower stress than before. This is sufficient to make the stress-strain curve obtained with a sensitive

extensometer slope away from the straight line that represents the elastic extension of the metal in its primitive state. The overstrained metal is thus imperfectly elastic within the range of primitive elasticity. If the second loading is not carried out immediately after unloading strain-ageing will proceed with time. This raises the resistance to deformation, and when the metal is loaded after a lapse of time its stress-strain curve approximates more closely to the original elastic curve. This is known as recovery. It takes place slowly at atmospheric temperature but more rapidly if the metal is heated. It has been the subject of many investigations among which may be mentioned those of Muir (59), Dalby (60), and Van Den Broek (61).

HEATING AFTER DEFORMATION

When metals are heated after deformation at atmospheric temperature the changes that follow distortion are accelerated and their progress depends on the time and temperature of heating and the amount of deformation. In general, deformation at atmospheric temperature produces an increase in resistance to it (i.e. in hardness), and according to the nature of the metal, the time and temperature of heating, and the original amount of deformation, the heating operation may produce an increase or decrease in hardness when the metal is tested at atmospheric temperature. All the metals that can be hardened by deformation can be softened by heating and this is an important industrial operation known as annealing. In general, the ultimate effect of annealing is to reduce the hardness to what it was before deformation, i.e. to eliminate strain-hardening, and an operation that leads to this is sometimes described as full annealing to distinguish it from one in which the strain-hardening is only partially eliminated. Experiments on the effects of deformation and heating are usually begun with the metal in a fully annealed condition so as to eliminate the influence of previous deformation, and the cycle is complete when the metal is again restored to this condition.

In studying this aspect of the subject four variables have to be taken into account—the metal, the amount of deformation, the temperature of heating, and the time of heating. Furthermore, in addition to the time during which the metal is maintained at a given temperature, that occupied in reaching it must be considered, and this becomes more important as the temperature increases. Pronounced increases in the hardness of iron and steel may be expected to result from the acceleration of strain-ageing by heating. Increases of less magnitude may be anticipated in other metals, but the most conspicuous effect of heating them is the reduction and elimination of strain-hardening as a result of recrystallization.

Examples of the effect of heating after deformation may now be considered.

Fig. 75 shows the effect of time and temperature on the maximum tensile strength of a steel containing 0.75 per cent. of carbon severely deformed at atmospheric temperature (62). Some 0.25-in. diameter rod of this steel was reduced in diameter by wire-drawing until its maximum tensile strength was raised to 100 tons per sq. in. Specimens of this wire were then heated for various times at the temperatures shown. They

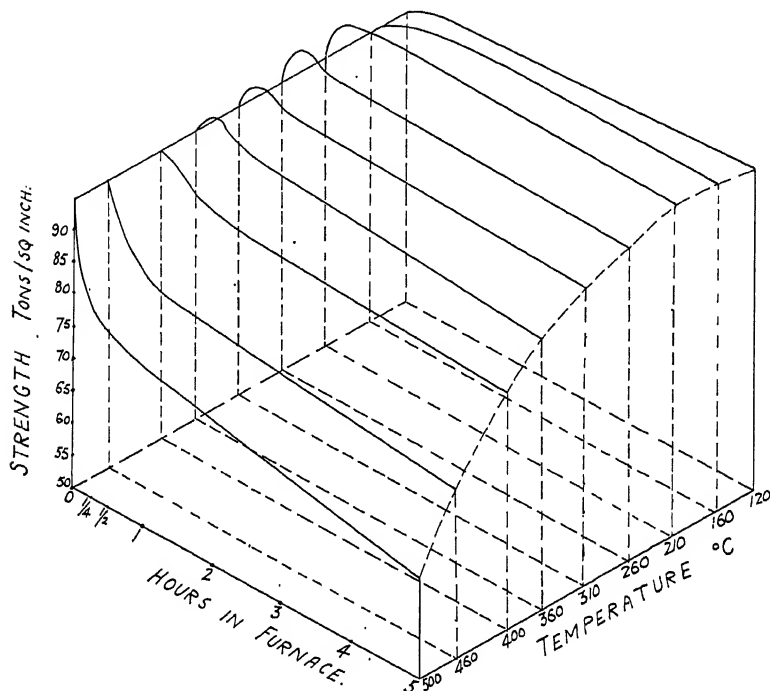


FIG. 75. Three axes diagram showing effect of time and temperature on tensile strength of cold-drawn wire. (*Royal Technical College Metallurgical Club Journal.*)

were then tested in tension at air temperature. At the lower temperatures the tensile strength increased with time just as it does at atmospheric temperature, and no subsequent decrease in strength was observed within the period of 5 hours which was the maximum time used in these experiments. It is evident, however, that had the time of heating been prolonged a decrease in strength would have been observed in the severely deformed material at the temperatures of 120° and 160° C. At 210° C. the strength rose to a maximum in 15 minutes and then began to decrease. As the temperature was further raised the maximum hardness was reached in less time, and the subsequent softening proceeded with greater rapidity. The shortest time of heating used was 15 minutes. After heating for this time at 400° C. the maximum on the time-hardness curve had already been passed, and the strength decreased continuously at this and all higher temperatures. Although

no increase in strength is shown in the strength-time curves for temperatures above $360^{\circ}\text{C}.$, it is probable that had the shortest time of heating been reduced to 1 minute or less, maxima would have been observed on some of them. When, however, the temperature was raised to about $500^{\circ}\text{C}.$, it seems likely that the conditions producing a higher tensile strength would be passed before it was reached. It will be observed

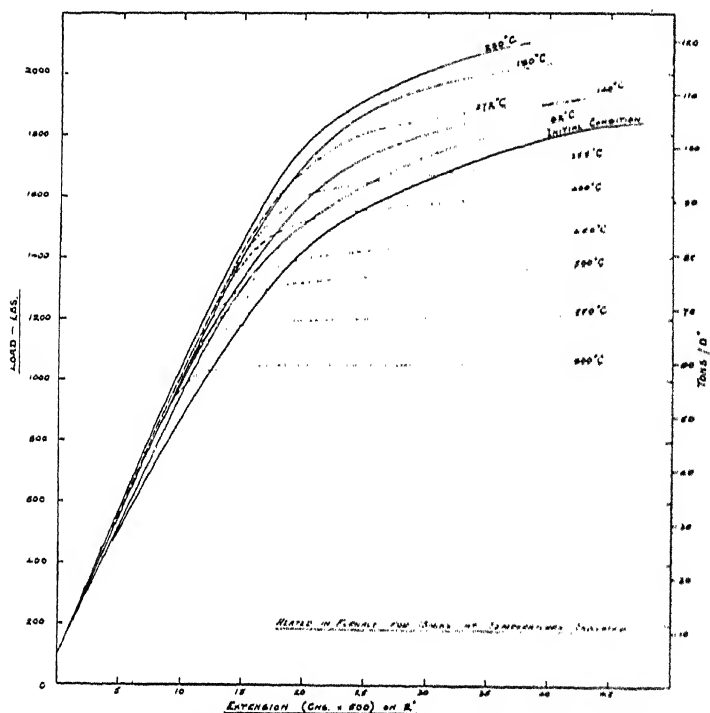


FIG. 76. Showing the effect of reheating on the stress-strain curve of cold wire. (Royal Technical College Metallurgical Club Journal.)

that the time taken to reach the maximum hardness decreases as the temperature is raised and that the maximum hardness is greater the lower the temperature. This latter feature is an important characteristic of all cases in which the hardness of metals is increased by heating.

Fig. 76 shows the effect of heating for 15 minutes at various temperatures on the load-extension curve of the wire described above. The curve marked 'Initial condition' refers to the wire after deformation and before heating. On heating at temperatures up to $230^{\circ}\text{C}.$ the curve becomes steeper, i.e. the cold-worked metal recovers its elasticity. Heating at higher temperatures produces no change in the slope of the curve at low loads, although the load at which marked yielding takes place is progressively reduced. The specimens represented by full lines

broke at the ends of the curves shown, while those represented by the broken lines underwent further extension before fracture.

Rees (63) studied the effect of heating a heavily deformed chromium-vanadium steel wire for 1 hour at temperatures between 100° and 600° C. His results are shown in Table 18. The limit of proportionality was determined with a Berry strain gauge which could be read to 0.00004 in. and a mirror extensometer that could be read to 0.000057 in.

TABLE 18

Effect of Heating on Cold-drawn Wire

(Carbon 0.42%, Chromium 1.11%, Vanadium 0.2%)

Heating temp. ° C.	Limit of proportionality		Yield-point tons/sq. in.	Tensile stress tons/sq. in.	Elongation % on 2 in.	Brinell hardness number
	Berry strain gauge	Mirror extensometer				
As drawn	45	26	90	107	2.5	418
100	46	32	95	109	1.0	415
200	74	43	102	111	3.0	428
250	86	..	111	114	2.0	457
300	88	64	108	110	4.0	448
400	80	61	102	102	4.0	444
450	78	..	95	97	5.5	426
500	73	56	90	90	6.0	408
550	69	..	86	86	6.0	392
600	41	44	54	54	13.0	268

In similar experiments on a carbon steel wire he found that the tensile strength reached a maximum after heating at 200° C. for 1 hour. This agrees with the results shown in Fig. 75. All these results apply, however, to heavily deformed metal, and when the amount of deformation is less, higher temperatures or longer times are necessary to obtain the maximum increase in hardness and cause the softening stage to be entered. Thus Tapsell (64), in an investigation of the effect of time and temperature on the properties of cold-worked Armco iron found the hardness to increase at all temperatures between 240° and 390° C. Even after 100 days at 340° C. and 30 days at 390° C. the metal did not show any tendency to soften. At 440° C., however, after a slight initial increase in hardness, softening began and proceeded slowly with time.

When heated after deformation non-ferrous metals do not exhibit such pronounced increases in hardness. Of the metals themselves nickel is the only one that exhibits this phenomenon in a marked degree, but many examples are to be found in the alloys of copper. On p. 1393 the heating of cold-worked copper-nickel alloys to obtain an increase in the limit of proportionality and tensile strength is described, and in Figs. 533 to 539, pp. 1297 and 1298, the hardening of brass by heating after deformation is illustrated. In each of the figures Nos. 533 to 538 the

curves *A*, *B*, and *C* refer respectively to metal reduced in area 20, 40, and 95 per cent. by wire-drawing. Curve *A* in Fig. 533 shows that at 200° C. metal that has been wire-drawn to a reduction in area of 20 per cent. undergoes no change in 220 minutes. Curves *B* and *C* show that metal reduced in area 40 and 95 per cent. increases in hardness. At 300° C. (Fig. 534) curve *A* shows a slight decrease in hardness, curve *B* an increase followed by a decrease, while curve *C* shows a rapid decrease. At 350° C. and all higher temperatures the three curves show a decrease in hardness that proceeds more rapidly as the temperature is raised. This set of figures shows that increasing the amount of deformation

lowers the temperature or decreases the time required to obtain the maximum increase in hardness.

The most conspicuous effect of heating non-ferrous metals after deformation is the elimination of strain-hardening as a result of recrystallization. As shown in Fig. 511 for copper and Fig. 539 for brass, this change begins slowly, then proceeds more rapidly and finally becomes slow again. Furthermore, it begins at a lower temperature and proceeds more rapidly as the amount of de-

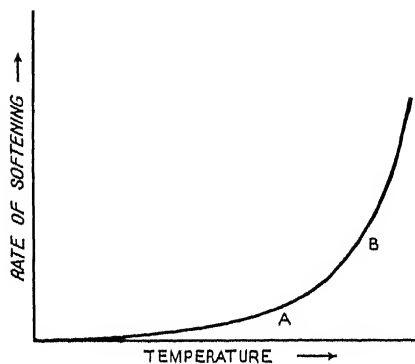


FIG. 77. Rate of softening against temperature.

formation is increased. This is also shown in Figs. 511 and 539 in which the various curves refer to different amounts of deformation. In the experiments on which these figures are based a constant time of heating at a series of different temperatures was employed. As a result the effect of the time of heating is not taken into account. In Fig. 510 an attempt is made to illustrate the relations between the three variables, deformation, time, and temperature. The different amounts of deformation are tabulated at the left-hand side of the figure. The various times of annealing are shown along the top. Each little square represents a specimen subjected to a given amount of deformation and annealed for a given time. The number in it shows the temperature at which softening began. It is apparent that in the case of copper the temperature at which softening began decreased as the amount of deformation and the time of heating increased.

Although the duration of heating after deformation influences the temperature at which softening occurs, an increase in time is not by any means equivalent to an increase in temperature. The curve connecting rate of softening with temperature is of the form shown in Fig. 77. At low temperatures the rate increases slowly, and then at *A* begins to increase much more rapidly. During continuous heating softening will

always occur in the range of temperature between *A* and *B*, and the same applies to short periods of heating at a series of rising temperatures. Pilling and Halliwell (65) carried out an extensive investigation on the softening of copper and some of their results are shown in Table 19. It will be observed that the rate of softening is greater in the case

TABLE 19

Softening of Cold-rolled Copper determined by Cold Tensile Tests subsequent to Annealing (Pilling and Halliwell)

	Annealing temperature ° C.	Annealing time	Softening %	Time required for complete softening
Initial reduction by cold rolling = 53.2%	100	285 days	9.1	310 years
	100	359 "	4.9	900 "
	150	11 "	11.8	9.1 "
	175	25 hours	9.4	430 days
	200	1 "	4.5	33 "
	225	5.2 "	70.0	104 hours
	250	30 min.	70.0	10 "
	300	2 "	70.0	40 min.
Initial reduction by cold rolling = 71.2%	100	285 days	12.6	223 years
	100	359 "	12.1	290 "
	150	11 "	33.3	2.7 "
	175	12 hours	17.8	96 days
	200	1 hour	19.0	10.4 "
	225	68 min.	70.0	23 hours
	250	8.1 "	70.0	2.7 "
	300	37 sec.	70.0	12 min.

of the more heavily cold-worked material, that it is extremely slow at temperatures below 150° C. and very rapid above 250° C. The times for complete softening at temperatures above 200° C. were actually measured, but the corresponding figures for temperatures below 200° C. were calculated on the assumption that the law of softening was the same at all temperatures. If correct, they indicate that if copper which has been reduced 71 per cent. can be completely softened at temperatures below 200° C., the operation would take a long time. The same investigators also determined the time required for complete softening at 250° C. of copper originally cold-worked to different extents. Their figures are as follows:

<i>Percentage reduction by cold rolling</i>	<i>Time for complete softening</i>
23.8	2,000 hours
53.2	10 hours
71.2	2.7 hours

DEFORMATION AT DIFFERENT TEMPERATURES

In the foregoing sections the relations between the factors considered have been simplified by dealing with conditions under which it is unnecessary to take them all into account at the same time. Such conditions are actually realized and have both practical and theoretical importance. They have not been assumed in order to simplify description. In this section, however, it is necessary to deal with conditions under which the effects of deformation, time, and temperature all operate at the same time.

The results obtained in ordinary tensile tests at different temperatures will be considered first. In general, the limit of proportionality,

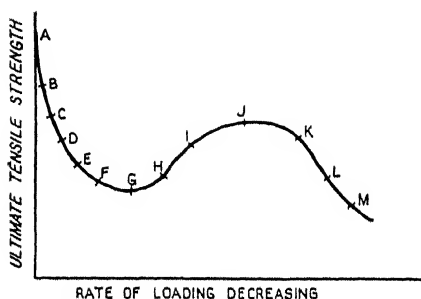


FIG. 78. Ultimate tensile strength against rate of loading.

yield-point, and ultimate tensile strength should decrease as the temperature of testing is raised. So far as the first two are concerned this statement is approximately true, but it is far from true when applied to the ultimate tensile strength when the metal under consideration undergoes substantial strain-ageing. Fig. 72 shows the relations between the tensile strength and the rate of loading. It applies particularly to

iron and steel in which strain-ageing is pronounced. In other metals the bulge *CDEF* is always much smaller and is frequently completely absent. By suitably adjusting the scales it may be made to apply to any temperature. In order to do this the curve must be altered in the following way as the temperature it is supposed to represent rises:

1. The whole curve must be lowered on the tensile strength scale.
2. The relative magnitude of the bulge must be reduced.
3. The time scale must be opened considerably in order that a few minutes at, e.g., 350° C. will be equivalent to many years at atmospheric temperature.

A similar curve is shown in Fig. 78. Subject to the above alterations with rising temperature it may be considered to represent the relations between the ultimate tensile stress and the rate of loading at any temperature between -180°C. and 700°C. It may now be used to illustrate the effect of testing at different temperatures, and for this purpose the most important point to bear in mind is the change in the time scale with temperature. Thus if a series of specimens is tested at the same rate at a series of rising temperatures, this rate may correspond to point *B* on the curve connecting strength and rate of loading at the lowest temperature, to point *C* for the next temperature, to point *D* for the next temperature, and so on. It follows therefore that the curve obtained

by plotting the tensile strengths obtained at different temperatures against temperature will be of the same form as that shown in Fig. 78.

The above may be explained in another way as follows: The portion A to G of the curve in Fig. 78 is due to the fact that the deformation produced by a given stress increases with the time for which it is applied. The portion G to L is due to strain-ageing increasing the resistance to deformation, and the portion beyond L is due to recrystallization decreasing it. The general tendency is for the tensile strength to decrease with rising temperature as a result of (1) the decreasing resistance to deformation, (2) the increasing effect of time on deformation, and (3) the effect of recrystallization. This tendency is opposed, however, by strain-ageing, and when the conditions are such that this proceeds at a rate similar to the rate of loading, it produces either a retardation in the decrease of strength with temperature or an actual increase in the tensile strength.

Now if the tensile strength-rate of loading curves could be determined for a series of temperatures and plotted in a three-dimensional diagram they would form a surface connecting tensile strength, rate of loading, and temperature. If the tensile strength axis was vertical, this surface would appear in plan as shown in Fig. 79, in which GG' and JJ' represent respectively the variations with temperature of the positions of the minimum and maximum on the strength-rate of loading curve. Lines such as XX' , YY' , and ZZ' represent given rates of loading, and it is clear that as the rate is decreased, the minimum and maximum on the curve connecting tensile strength with temperature will occur at lower temperatures.

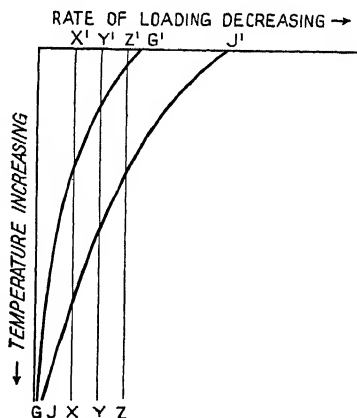


FIG. 79. Plan of strength, time, temperature surface.

Some examples of the effect of temperature and rate of loading may now be considered. Figs. 80 and 81 plotted from data obtained by Inokuty (66) show the relations between tensile strength and temperature for several metals tested at almost the same rate. In the tensile test iron does not display low temperature brittleness above $-200^{\circ}\text{C}.$, and the tensile strength, which is a maximum at $-185^{\circ}\text{C}.$, decreases progressively as the temperature is raised from $-185^{\circ}\text{C}.$ to air temperature. Just below zero, however, the rate of decrease of strength begins to diminish; at about $80^{\circ}\text{C}.$ there is a point of inflexion on the curve and thereafter the strength increases as the temperature of testing is raised and reaches a maximum at $250^{\circ}\text{C}.$ Above this temperature the strength begins to decrease, but even at $500^{\circ}\text{C}.$ it is considerably higher than it would have been had the rate of decrease observed

between $-185^{\circ}\text{C}.$ and $0^{\circ}\text{C}.$ been maintained. The other curves in Figs. 80 and 81 show that strain-ageing affects the tensile strength of different metals to different extents, and over different ranges of temperature. Thus the normal decrease in the strength of copper is retarded between $0^{\circ}\text{C}.$ and about $450^{\circ}\text{C}.$; of aluminium from $-100^{\circ}\text{C}.$ to about $+200^{\circ}\text{C}.$;

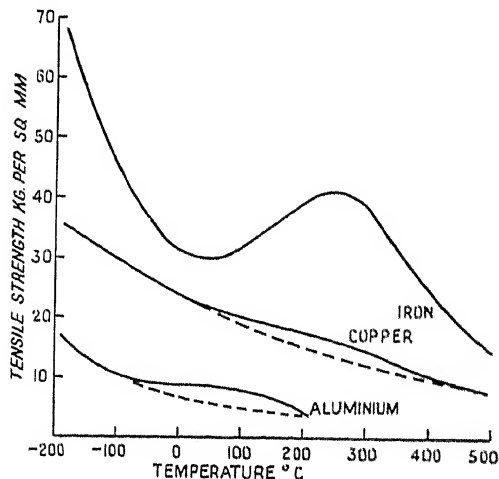


FIG. 80. Effect of temperature of testing on tensile strength of iron, copper, and aluminium.

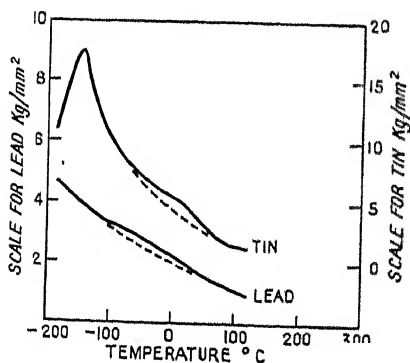
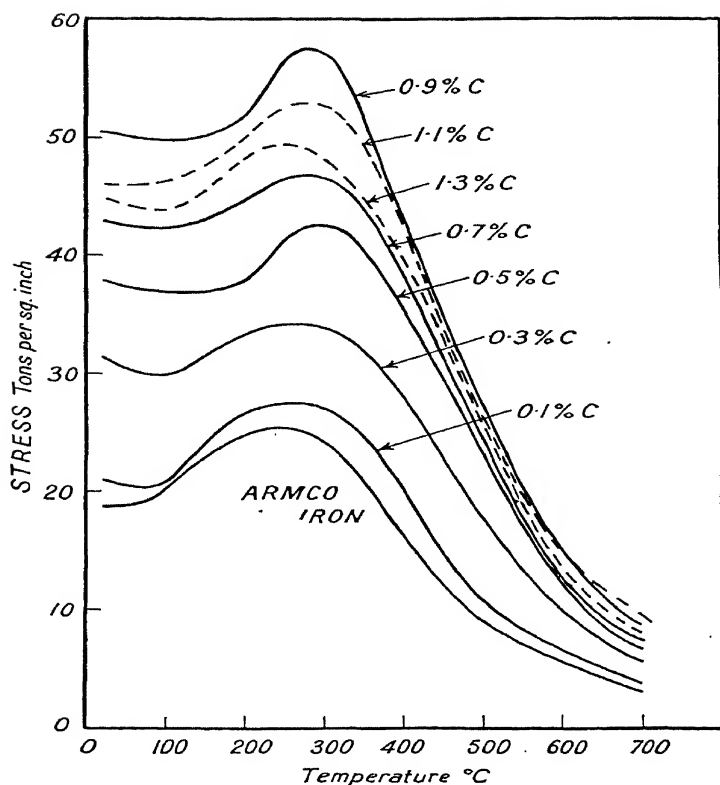


FIG. 81. Effect of temperature of testing on tensile strength of lead and tin.

of lead from $-150^{\circ}\text{C}.$ to $+50^{\circ}\text{C}.$; and with tin, which exhibits low temperature brittleness below $-150^{\circ}\text{C}.$, it is retarded between $-80^{\circ}\text{C}.$ and $+80^{\circ}\text{C}.$ Fig. 82 shows the variations in tensile strength with temperature of Armco iron and a series of carbon steels (64). The high tensile strength in the range between 200° and $350^{\circ}\text{C}.$ is accompanied by low elongation and reduction in area as shown in Fig. 83, and this is known as the range of 'blue brittleness' because in it blue oxide films



g. 82. Effect of temperature of testing on tensile strength of Armco iron and a series of carbon steels. (Tapsell, *Creep of Metals*.)

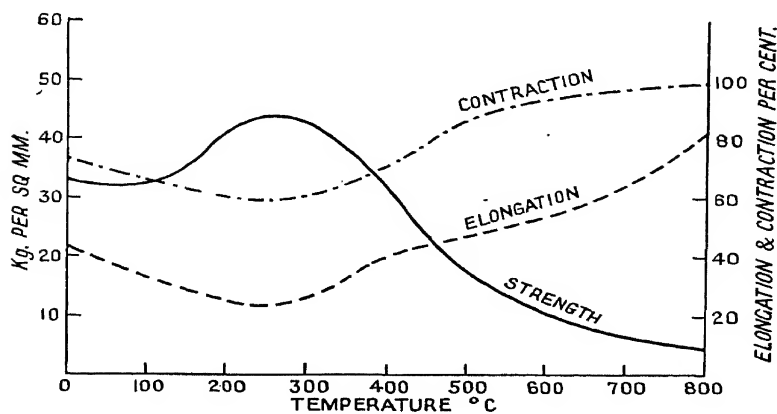


FIG. 83. Effect of the temperature of testing on the tensile strength, elongation, and contraction in area of steel.

are produced on the polished surface of iron. If steel is tested in this range, its tensile strength is high and its elongation low. If it is deformed at air temperature, heated into this range, and then tested at air temperature, the same brittleness is observed, particularly if the impact test is used.

It has been shown by Welter (67) and others that all plain carbon steels and those containing small amounts of alloying elements show a maximum on the curve connecting tensile strength and temperature; but whereas in the case of carbon steels the maximum reached in the range 200–300° C. is higher than the strength at atmospheric temperature, in alloy steels it is frequently lower. In steels containing high proportions of alloying elements and in non-ferrous metals and alloys there is no absolute rise in the tensile strength in the range in which it is influenced by strain-ageing. All that is observed is a retardation in the rate of decrease of strength with rising temperature. Examples of this are furnished by the curves of copper, aluminium, tin, and lead in Figs. 80 and 81. The curves in Figs. 541 and 542 showing the variation with temperature of the tensile strength of two types of brass also show a retardation in the rate of decrease in strength with rising temperature; in this case in the range from –100° C. to about +500° C. A similar effect in Monel metal is shown in Table 212, p. 1395. It is thus evident that although non-ferrous metals do not exhibit the effects of strain-ageing to the same extent as iron and steel, this change frequently gives rise to appreciable increases in strength which are particularly well shown on curves such as those in Figs. 80 and 81.

As already explained, the range in which the increase in strength arising from strain-ageing occurs should move towards lower temperature as the rate of loading is decreased. This has been demonstrated by Greaves and Jones (68) and Lea (69). The former determined the temperature-strength curves for Armeo iron over the range 80° C. to about 500° C. using two different rates of loading which enabled the tests to be completed in 10 minutes and 2 hours respectively. With slow loading the maximum on the curve occurred at 180° C., with rapid it occurred at 350° C. Lea performed similar experiments on mild steel and obtained a maximum at 200° C. when the tests were of 2 hours' duration and at 400° C. when they were of 10 minutes' duration.

The relations between strain-ageing, temperature, and mechanical properties may be further illustrated by considering the case of a metal deformed to different extents at elevated temperatures and then tested at atmospheric temperature. A convenient way of studying this is as follows: A series of specimens is broken in tension at different temperatures, and then at atmospheric temperature hardness determinations are made at a number of points between the fracture and one end of the specimen. The amount of deformation to which each specimen is subjected decreases as the distance from the fracture increases, so that when the hardness determinations made on each specimen are plotted

against the reduction in area at the points where the determinations were made, curves are obtained showing, for each temperature, the relations between degree of deformation and induced hardness. In such experiments time is not taken into account, but the induced hardness is influenced by the amount of deformation and the relations between this and the changes that follow deformation. A series of experiments on the above lines was carried out by Tapsell (64), and the results obtained are

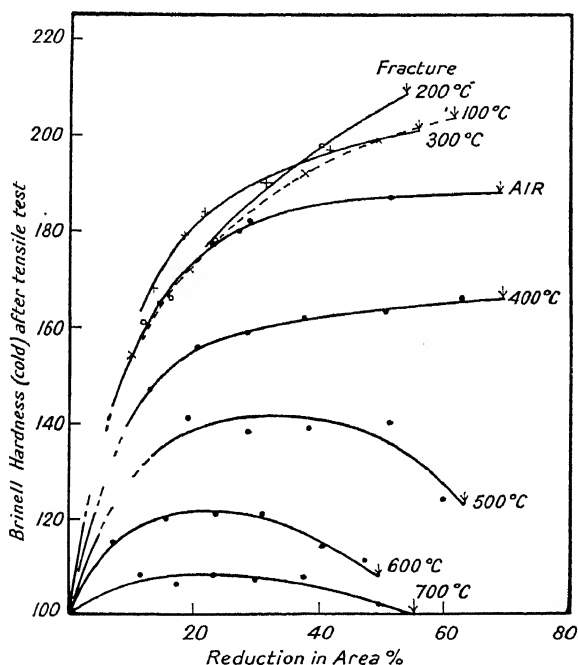


FIG. 84. Hardness (cold) along specimens of Armco iron broken at different temperatures. (Tapsell, *Creep of Metals*.)

shown in Fig. 84 in which each curve represents the connexion between the amount of deformation and the induced hardness for a particular temperature. It will be observed that as the testing temperature is raised from atmospheric to 200° C. the hardness increases at points reduced in area more than 20 per cent., but not at points reduced less than this. At 300° C. the hardness at points reduced in area more than 35 per cent. begins to decrease while that at points reduced less than this continues to increase. Above 300° C. there is a progressive decrease in hardness at all points, but the extent of this is greatest at the points which have sustained the most reduction. The general inference from the results shown in Fig. 84 is that the changes that follow deformation proceed more rapidly as the temperature and amount of deformation are increased.

It remains to consider the effect of prolonged loading at different temperatures. In dealing with tensile tests at different temperatures account is taken of the relations between rate of loading, deformation, and the changes that follow it, but the relations between the amount of deformation and the rate of the changes that follow are not considered. In the experiments just described temperature and the relations between deformation and the changes that follow are taken into account, but time is not considered. In dealing with prolonged loading at different temperatures all factors operate at once. Thus, when a given load is applied to a specimen at a particular temperature, a certain amount of deformation is produced at once, and it then continues with time at a rate that depends on the metal, the temperature, and the load. The initial deformation initiates the changes that follow it. These proceed at a rate that depends on the metal, the temperatures, and the amount of deformation, and they tend to retard or facilitate deformation with time according to whether they increase or decrease resistance to it. As, however, these changes involve an increase followed by a decrease in resistance to deformation, they may retard deformation at first and facilitate it later.

It is obviously impossible to follow out step by step all that takes place when a metal is subjected to the prolonged application of a constant load at a particular temperature, and fortunately it is possible to describe the observed behaviour without doing this. We may begin by considering the conditions realized under prolonged constant tensile loads at atmospheric temperature without taking account of the changes that follow deformation. As this has already been dealt with in some detail under 'Deformation and Time', all that is necessary is to bring together the relevant conclusions from that section.

When a test-bar is subjected to progressive tensile deformation, its resistance to it first increases and then decreases. When the deformation is produced by a progressively increasing load, the point at which its resistance to deformation is a maximum is known as the ultimate tensile strength. When a constant load is applied, deformation continues with time. If the load is sufficient to deform the bar to its point of maximum resistance to deformation, then deformation with time proceeds at an increasing rate. If, however, the load does not immediately produce this effect, then deformation with time proceeds at a decreasing rate. So long as deformation is taking place with time, however, the bar may eventually be deformed to its point of maximum resistance, and thereafter deformation will proceed at an increasing rate to fracture. Thus the general curve connecting time and deformation under constant load has the form shown in Fig. 70. The point F , at which the rate of deformation with time begins to increase, may be reached in hours, days, weeks, months, years, or after an infinite time. As the rate of deformation decreases with time until the point F is reached, the minimum rate of deformation is attained just before the rate begins to increase, and this

minimum rate decreases in magnitude as the time required to reach it increases.

Actual investigations of deformation under prolonged load are necessarily of limited duration, and this limit may be set by the fact that after a certain time the rate of deformation is still decreasing becomes too small to measure. Alternatively, it may be determined by the necessity of completing the tests within a certain period. If we consider the effect of different loads applied for a limited period we find that (1) the amount of deformation produced on first application, and (2) the initial rate of deformation with time, will increase with the magnitude of the load, while (3) the rate at which the rate of deformation decreases, and (4) the time taken to reach the minimum rate, will decrease with increase in the magnitude of the load. Thus, if we determine a series of time-deformation curves under different loads, we obtain a set such as those shown in Fig. 85. In this figure the ordinate represents extension and the abscissa represents time. The seven curves shown are therefore extension-time (or creep) curves for different loads. For the present purpose the fact that the first portions of the curves are supposed to be experimental and the remainder hypothetical may be neglected. Each curve shows that a certain extension occurs on first application of the load. Following this, extension takes place at a diminishing rate until a point of inflexion is reached. Thereafter extension proceeds at an increasing rate. The initial extension increases with the load and so does the initial rate of creep. But the rate at which the rate of creep diminishes, increases as the load decreases, and so does the time taken to reach the minimum rate. The minimum rate is indicated on each curve by a point and these points are connected by a curve which indicates how the time taken to reach the minimum increases as the load decreases.

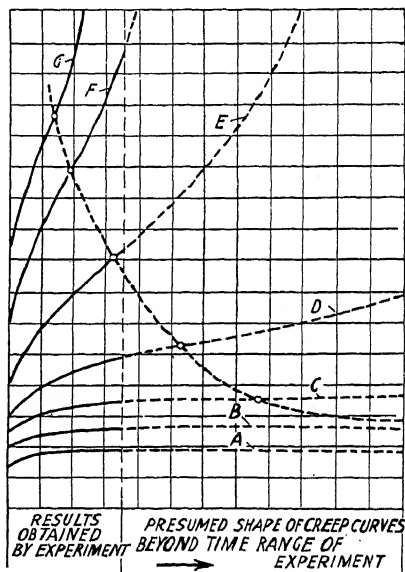


FIG. 85. (Metal Treatment.)

If we consider the effect of a given load at a series of rising temperatures (neglecting the changes that follow deformation), we find that (1) the amount of deformation produced on first application and (2) the initial rate of deformation with time will increase with rising temperature, while (3) the rate at which the rate of

deformation decreases, and (4) the time taken to reach the minimum rate, will decrease with rising temperature. Thus, if we determine a series of time-deformation curves under the same load at different temperatures, we again obtain a set like that shown in Fig. 85.

When iron and steel are subjected to prolonged tensile loads at atmospheric temperature, the rate of deformation with time will not reach the stage at which it begins to increase, unless the load is very close to the ultimate tensile strength as determined in a short-time test. Thus, although a family of curves such as are shown in Fig. 85 might theoretically result, only the lower curves are actually obtained. At temperatures above 350°C ., however, deformation with time proceeds to a much greater extent, and a load considerably below the ultimate tensile stress determined in a short time test may produce deformation at a decreasing rate to such a degree that the point of maximum resistance to deformation is passed in a reasonable time, and deformation at an increasing rate begins. In this range a set of curves such as are shown in Fig. 85 may be obtained by applying different loads at the same temperature or the same load at different temperatures. In the pure metals, deformation with time under constant load becomes important at progressively lower temperatures in the order iron, nickel, copper, aluminium, zinc, lead, and tin, and in the last three it influences their behaviour at atmospheric temperature in a pronounced degree. There are, however, many alloys based on iron and nickel in which the temperature at which deformation with time becomes important is much higher than in pure iron or ordinary steel.

The significance of creep curves such as are shown in Fig. 85 may be readily appreciated by comparing them with load-extension curves such as that shown in Fig. 27. A typical tensile creep curve shows that extension proceeds at a diminishing rate until a minimum is reached, and then at an increasing rate to fracture. The time taken to reach the minimum depends on the metal, the temperature, and the stress. It may vary from a few seconds to a few million years, and long before the minimum is reached the rate of creep may become too small to be detected even with the most sensitive instruments. Similarly, after the minimum is passed, the time that elapses before fracture occurs may be of any conceivable length, but the fact remains that the characteristic feature of creep curves is extension at a decreasing rate to a minimum followed by extension at an increasing rate to fracture. A typical load-extension curve shows that extension takes place under an increasing load till a maximum is reached, and then under a decreasing load to fracture. In each type of curve the form of the first part is determined by the fact that the resistance to deformation is increasing, i.e. it takes place under an increasing load or at a diminishing rate. The form of the second part depends on the fact that the resistance to deformation is decreasing, i.e. it takes place under a decreasing load or at an increasing rate. Finally, in each type of curve there is a point of maximum

resistance to deformation which is represented by the ultimate tensile stress and minimum rate of creep respectively. Once it is appreciated, as explained in an earlier section, that stress and time are to some extent equivalent, in the sense that extension may continue with increasing time although the resistance to deformation is increasing just as it does with increasing stress, the relations between time-extension and load-extension curves are evident. All the features of creep curves can be deduced from load-extension curves, and in fact both types of curves are really lines transversing the load-time-extension surface in different directions. In creep tests, necking begins when the point of minimum rate of creep is past, just as it begins at the ultimate tensile strength in load-extension tests.

The question now arises as to how the behaviour of metals under prolonged loads is affected by the changes that follow deformation. It is obvious that strain-ageing will tend to increase resistance to creep, while recrystallization will tend to decrease it. In a given case of a metal deforming at a decreasing rate under a constant load it is impossible to determine whether the decrease in the rate of deformation is due to the relations between time and deformation, to strain-ageing, or the combined effect of both. In some cases it is equally impossible to determine whether deformation at an increasing rate is due to the relations between time and deformation, to recrystallization, or both; but in others recrystallization may be shown to be in operation by studying the changes in microstructure. There can be no question that strain-ageing and recrystallization influence the quantitative aspects of creep. What has to be considered, however, is whether they modify or control the general aspects of the behaviour of metals under prolonged tensile loads. Is there, e.g., any feature of typical creep curves such as are shown in Fig. 85 that cannot be explained without considering these changes? It is evident from what has been said that there is not, unless deformation at a decreasing rate with time is identified with strain-ageing. In so far as tensile loading is concerned all that can be said about the changes that follow deformation is that strain-ageing increases the resistance to deformation, and thus raises the load, temperature, or time necessary to attain the point at which deformation at an increasing rate begins, while recrystallization decreases resistance to deformation, and thus reduces the load, temperature, or time necessary to attain the point at which deformation at an increasing rate begins. There is nothing to be gained by endeavouring to distinguish the separate effects of strain-hardening, strain-ageing, and recrystallization. When time and stress are acting simultaneously, these three processes are merged. On the first application of the load a certain amount of strain-hardening is produced. Thereafter, deformation, strain-hardening, strain-ageing, and recrystallization all proceed concurrently at mutually dependent rates. All that matters, however, is whether, to what extent, and for how long the resistance to deformation increases, and in so far as this is

concerned all the changes that affect resistance to deformation may be grouped together.

The conditions are different when we consider stresses other than tensile stress, e.g. compression, torsion, or bending. Under tensile loads deformation with time changes from a decreasing rate to an increasing rate when the point of maximum resistance to deformation is passed. Strain-ageing and recrystallization influence the position of this point in terms of load, temperature, and time, but its existence does not depend on them, and the general behaviour of metals under prolonged loads would be the same if these changes did not occur. Fundamentally, the existence of the point of maximum resistance to deformation depends on the relations between strain-hardening and reduction in cross-sectional area as shown in Fig. 29. When, however, metals are deformed by compression, bending, or torsion, the cross-sectional area does not diminish as deformation proceeds. Thus there is no point of maximum resistance to compression, bending, or torsion, and the resistance to deformation increases progressively as deformation proceeds. Under such conditions deformation with time is controlled by different factors from those that apply to tensile loads. As far as the relations between time and deformation are concerned, a specimen bending under a constant load must continue to deform at a decreasing rate. Strain-ageing tends to accentuate this decrease in rate, and whether it operates or not, the rate of deformation will soon become negligibly small. If, however, recrystallization is taking place, deformation may continue, for each small amount of deformation is followed by a decrease in resistance to deformation, which permits a further small amount of deformation, and so on. Thus the specimen continues to bend at a constant rate.

THE EFFECT OF TIME AND TEMPERATURE ON THE MECHANISM OF DEFORMATION AND FRACTURE

This section is based mainly on the investigations of Hanson and Wheeler (23) and Jenkins and Mellor (70), who studied the effect of time and temperature on the deformation of aluminium and iron respectively. In the first of these investigations specimens composed of single crystals, small numbers of large crystals, and large numbers of small crystals, were subjected to different conditions of straining at normal and elevated temperatures. When a rapid rate of straining was employed so as to produce fracture in a few minutes, the mechanism of flow and fracture was as described in Chapter III. When deformation was slow, however, and several days were required to produce fracture, definite changes in the behaviour of the metal were observed. In order to describe these it is convenient to divide the complete test under constant load into the three stages recognized by Hanson and Wheeler. As already explained, deformation under a constant load of sufficient magnitude to produce fracture within the period of the test involves (1) initial deformation

produced as the load is applied, (2) deformation with time at a decreasing rate, and (3) deformation with time at an increasing rate. Now it is evident that when instruments of a given sensitivity are used, the deformation at a decreasing rate may appear to cease at a certain point, and no further deformation be detected until the deformation at an increasing rate exceeds a certain minimum. Between these points no measurable deformation occurs, and Hanson and Wheeler divide creep into three stages as follows:

1. A period of primary extension during which deformation proceeds at a decreasing rate.



FIG. 86. After 210 hours under load at 250° C. Elongation 21 per cent. $\times 150$.
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2. A period during which deformation is very slow or even suspended.
3. A period during which deformation proceeds at an increasing rate to fracture.

During the first stage aggregates and single crystals behave similarly and deform by slip on crystallographic planes. The number of planes involved may, however, be so large that no microscopically visible slip-bands are produced. Deformation by slip without the formation of visible bands is a normal feature of the behaviour of polycrystalline specimens under prolonged load at elevated temperature. Fig. 86 shows the unetched surface of a specimen extended 21 per cent. under a stress of 1.4 tons per sq. in. applied for 210 hours at 250° C. Fig. 87 shows the unetched surface of a similar specimen rapidly extended by the same amount at the same temperature. In the former, slip-bands are absent and the crystal boundaries are developed to a pronounced extent. In the latter, slip-bands are plentiful and the development of the boundaries is much less marked. It might be inferred that the differences in level at the boundaries and the absence of slip-bands in Fig. 86 are the result of deformation by movement at the boundaries instead of by slip. It is evident that some movement at the boundaries has taken place, but the

deformation cannot wholly be attributed to this, for high-power examination under the microscope showed that the change in shape of the individual crystals was the same as that of the specimen as a whole, i.e. they were elongated in one direction and contracted in others to the



87. Strained rapidly at 250° C. Elongation 21 per cent.
(*Journal of the Institute of Metals.*)

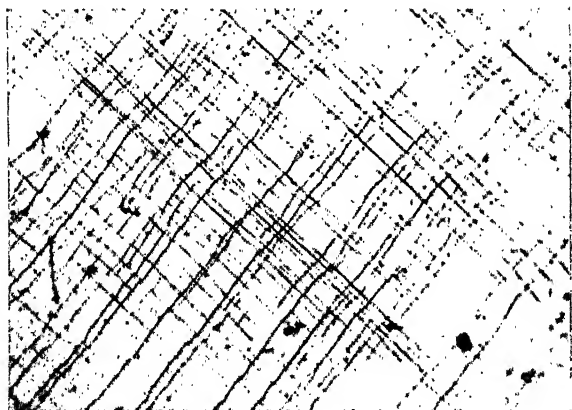


FIG. 88. After 41 hours under load at 250° C. Elongation 8½ per cent. \times
(*Journal of the Institute of Metals.*)

same degree as the test-piece. Under similar conditions single test-pieces exhibit microscopically visible slip-bands as shown in Fig. 88 which is the unetched surface of a single crystal extended 8 per cent. by the application of a stress of 1.4 tons per sq. in. for 41 hours at 250° C. In other experiments, however, Hanson and Wheeler showed that when they increased the load very slowly instead of applying a stress of 1.4 tons per sq. in. in a few minutes, then deformation could be produced without the formation of visible slip-bands.

During the second stage in which the rate of extension is extremely slow there is a marked difference in the behaviour of single crystals and aggregates. At 250° C. the density of aggregates slowly decreases as a result of the formation of incipient intercrystalline cracks, while in single crystals tested at this and other temperatures the only change observed is a slight increase in the intensity of the slip-band. During the third stage, in which deformation at an increasing rate occurs, the difference between aggregates and single crystals is even more marked. In aggregates this stage is accompanied by widening, propagation, and increase in the number of the cracks, which first appear at crystal

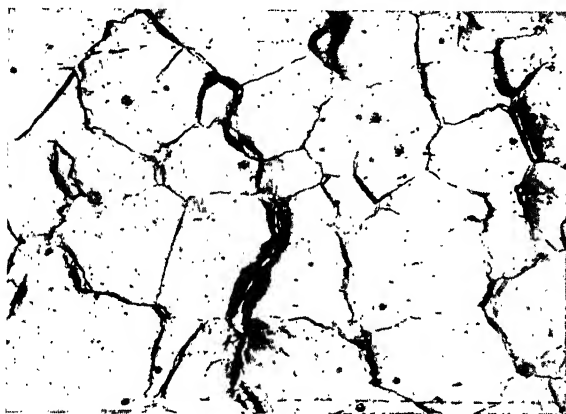


FIG. 89. Specimen extended 11.8 per cent. in 280 hours at 250° C. $\times 150$.
(*Journal of the Institute of Metals.*)

boundaries, but may spread either along boundaries or through crystals (Fig. 89). Thus the metal deforms without much change in shape of the crystals, the density decreases, and fractures that are either wholly or partly intercrystalline result. In the case of single crystals at all temperatures up to 400° C. and in aggregates at air temperature, the third stage in creep is accompanied by a resumption of slip. The slip-bands now formed are much thicker than those produced during the first stage, and the two kinds are clearly distinguished in Fig. 90 which shows the unetched surface of a single crystal specimen at the stage when necking began. Fracture ultimately takes place along the slip planes.

The results described above show that prolonged loading tends to produce substantial changes in the mechanism of deformation, and in the relations between deformation and fracture. So far as the mechanism is concerned the most important aspect is the production of considerable amounts of deformation without the formation of visible slip-bands. Hanson and Wheeler conclude that this type of deformation is the more readily produced (a) the slower the rate of straining, (b) the higher the temperature, and probably (c) the smaller the grain size. The effect of

time and temperature on the relations between deformation and fracture is even more striking. In the preceding portions of this chapter attention has been confined to deformation, and the failure of a metal under the prolonged application of a tensile pull has been described as if time and stress were interchangeable. In other words it has been assumed that we are dealing with the same phenomenon when we break a metal by progressively increasing the load, by the application of a large constant load for a short time, or of a small constant load for a long time. If this were true, it would follow that in the absence of strain-ageing effects the reduction in area at fracture should increase with the

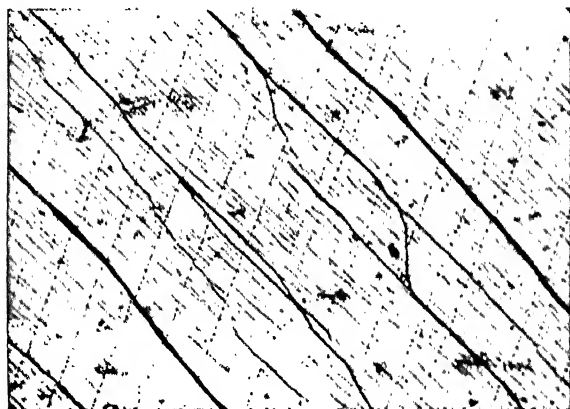


FIG. 90. Light slip-bands produced during early, and heavy bands produced during later stages of extension. $\times 150$.
(*Journal of the Institute of Metals.*)

temperature of testing. This is realized in some short-time tests as shown in Fig. 83. Under certain conditions it may also be realized in creep tests, but under other conditions quite different results arise from the influence of prolonged stress on the mechanism of fracture. Under the conditions of the experiments performed by Hanson and Wheeler prolonged stress produced a gradual disintegration of the metal either at the grain boundaries or on the surfaces where slip had previously taken place. Thus, in the case of the aggregates subjected to prolonged stress at 250°C . a certain amount of deformation first occurred, and then extension appeared to stop. After a certain time, however, instead of further deformation by slip taking place the specimens began to fracture. This shows that the breaking stress and the mechanism of fracture are directly affected by the time of application of a stress irrespective of the amount of deformation produced.

Some aspects of the effect of time on the relations between deformation and fracture are illustrated in Tables 20, 21, and 22, based on the results of Jenkins and Mellor. The tests were conducted *in vacuo* and the analyses of the materials concerned were as follows:

	<i>Swedish iron</i>	<i>Carbonyl iron</i>	<i>Armco iron</i>
Carbon . . .	0.017	0.016	0.016
Silicon . . .	0.05	under 0.002	0.006
Sulphur . . .	0.003	„ 0.0005	0.017
Phosphorus . . .	0.036	„ 0.0008	0.003
Manganese . . .	0.005	„ 0.005	0.030
Nickel . . .	nil	0.011	0.030
Chromium . . .	nil	nil	nil
Copper . . .	nil	under 0.002	0.07
Oxygen	0.016	0.175
Nitrogen . . .	0.006	0.003	0.003

TABLE 20

Tests on Armco Iron (in vacuo) at Different Temperatures with Different Rates of Straining

<i>Temperature ° C.</i>	<i>Creep load or ultimate tensile stress tons/sq. in.</i>	<i>Duration of test</i>	<i>Elongation %</i>	<i>Reduction in area %</i>
15	20.4	Short time	44	73
350	23.5	„ „	52	64
„	13.8	46 hours	60	75
450	15.1	Short time	61	81
„	5.9	41 days	36	33
550	8.6	Short time	55	88
„	5.9	2 hours	27	39
650	5.2	Short time	69	75
„	0.94	26.5 days	2	6
750	3.21	Short time	50	54
„	0.44	32.6 days	5	5
850	2.26	Short time	70	66
„	0.29	46 hours	11	20

TABLE 21

Tests on Carbonyl Iron (in vacuo) at Different Temperatures with Different Rates of Straining

<i>Temperature ° C.</i>	<i>Creep load or ultimate tensile stress tons/sq. in.</i>	<i>Duration of test</i>	<i>Elongation %</i>	<i>Reduction in area %</i>
15	18.2	Short time	47	94
750	2.49	„ „	105	98
„	0.5	26 hours	92	95
850	0.9	Short time	127	99
„	0.35	1.75 hours	100	97
950	2.51	Short time	146	99
„	0.35	19 hours	11	30

TABLE 22

on Swedish (Lancashire) Iron (in vacuo) at Different Temperatures with Different Rates of Straining

Temperature ° C.	Creep load or ultimate tensile stress tons/sq. in.	Duration of test	Elongation %	Reduction in area %
15	19.7	Short time	59	79
350	25.7	" "	34	56
"	15.8	27.5 days	29	74
450	16.2	Short time	83	78
"	5.8	26.1 days	55	82
550	10.45	Short time	90	88
"	3.9	18 hours	115	86
"	2.9	8.1 days	34	87
650	5.3	Short time	132	90
"	0.94	28.6 days	27	39
750	2.8	Short time	127	95
"	0.94	5 hours	80	79
850	1.55	Short time	112	97
"	0.30	46 hours	72	89

In considering these tables attention may be confined to the variations in reduction in area which are the best indication of the deformation that precedes fracture. In Armco iron (Table 20) the reduction in area in the short-time test increases from 73 per cent. at 15° C. to 88 per cent. at 550° C. and then decreases to 54 and 66 per cent. at 750° and 850° C. respectively. Presumably, in this material the influence of time and temperature in modifying the relations between deformation and fracture affects even short-time tests at temperatures above 550°. At 350° C. the reduction in area in the long-duration test is greater than in the short-time test. At all higher temperatures it is lower, particularly at 650° and 750° C. This shows the extent to which the relations between deformation and fracture may be modified by time at elevated temperatures. In Carbonyl iron (Table 21) the reduction in area in the short-time test increases slightly with temperature. In the long-duration tests at 750° and 850° C. the reduction in area is only slightly less than in the short-time tests. At 950° C., however, it is considerably less. In Swedish iron (Table 22) the reduction in area in the short-time test falls to a minimum at 350° C. and then increases progressively with the testing temperature to 850° C. At 350° and 450° C. the reduction in area in the long-duration tests exceeds that in the short-time tests. At 550° there is not much difference, but at 650°, 750°, and 850° C. the reduction in the long-duration tests is less than in the short-time tests. This is particularly marked at 650° C., probably as a result of the long time during which the specimen was under stress.

In describing the relations between deformation and fracture in Chapter III it was assumed that a metal has a certain breaking stress, and that it fractures when the resistance to deformation induced by

strain-hardening exceeds it. A metal that strain-hardens slowly must be drawn down to a fine point before the resistance to deformation exceeds the breaking stress. A metal that strain-hardens rapidly breaks when the amount of deformation at the point of fracture is considerably less. In general the amount of deformation (i.e. reduction in area) at the point of fracture increases as the rate of strain-hardening decreases. This may be called the normal relation between deformation and fracture. From it we can infer that when different metals are subjected to short-time tensile tests at atmospheric temperature those that strain-harden least will have the greatest reductions in area at the point of fracture. We can also infer that in the absence of strain-ageing effects the same metal tested at different temperatures with different rates of straining should show a greater reduction in area at higher temperatures and with slower rates of straining.

The normal relations between deformation and fracture are generally realized in short-time tests at atmospheric temperature, whereas departures are sometimes observed in short-time tests and commonly observed in long-duration tests at elevated temperatures. In other words, as the temperature or duration of the test is increased, the observed behaviour tends to depart to an increasing extent from the normal. The reason for this is that there is a direct relationship between stress and fracture, as a result of which a metal may break under a suitable combination of stress, time, and temperature without regard to previous deformation. This phenomenon is most clearly exhibited when a metal that behaves like a normal ductile metal in a short-time test at a given temperature breaks without much deformation in a long-duration test at the same temperature. These conditions are approximately realized in the case of Armco iron at 650° and 750° C. (Table 20). In general, however, normal and abnormal behaviour are not so clearly distinguished, and all kinds of combinations are possible as will be seen in Tables 20, 21, and 22, in which the extent of the departure from normal behaviour increases with the temperature, the duration of the test, and in passing from Swedish iron, through Carbonyl iron, to Armco iron.

The investigation of Jenkins and Mellor was much more extensive than that of Hanson and Wheeler. The experiments were carried out *in vacuo*, and in many of them the conditions were such that deformation was accompanied by recrystallization. Their report contains a large amount of information obtained in carefully conducted experiments, but for the present purpose it will suffice to refer to a few of their general observations.

In creep tests deformation can take place in three ways: (1) by slip on the crystallographic planes, (2) by movement at the grain boundaries, and (3) by movement beginning as slip or grain boundary changes and proceeding after the initial period by contemporaneous recrystallization of the strained material. Three types of recrystallization may be distinguished: (1) the replacement of the original deformed crystals by a

new generation, i.e. full recrystallization, (2) division of existing crystals into smaller units, i.e. sub-boundary recrystallization, and (3) crystal recovery leading to the partial elimination of strain-hardening without the formation of new crystals or subdivision of the original ones. The normal manner of failure in iron and mild steel fractured below 400° C. is by transcrystalline rupture. In long-duration tests at 400° C. Armco iron exhibits intercrystalline cracking, but no characteristic intercrystalline failure is found in the other materials at this temperature. In addition to slip other forms of movement can be seen on the surface of test-pieces. At temperatures higher than about 500° C., varying with different materials, there is on the surface a widening of transverse grain boundaries which develop into intercrystalline cracks for a crystal or so. These cracks show little tendency to spread into the material except in Armco iron. The tests on this metal also show that intercrystalline cracks may develop by internal separation of the grains. The mode of failure of mild steel at high temperature is not ascribable to a general intercrystalline form of cracking. Swedish iron shows ease of recrystallization, considerable ductility, but a marked tendency to form longitudinal fibres under the action of deformation. Armco iron is the least ductile of all the materials, and is characterized by a tendency to develop intercrystalline cracking at high temperatures. Carbonyl iron shows no tendency to split longitudinally into fibres, but is otherwise very similar in behaviour to Swedish iron.

When the normal relations between deformation and fracture are realized, the resultant rupture is generally transcrystalline. When fracture occurs as a direct result of a given stress acting for a given time at a given temperature, the rupture is either wholly or partly intercrystalline, and in any case begins by the crystals separating at the boundaries. As transcrystalline fractures are generally obtained at low temperatures, and intercrystalline fractures become more common at high temperatures, the conception of the equicohesive temperature introduced by Jeffries (17) has been widely accepted. According to this view the boundaries are stronger than the crystals at low temperatures, the crystals are stronger than the boundaries at high temperatures, and at some particular intermediate temperature both are equally strong (i.e. equicohesive). If it is recognized that the equicohesive temperature falls as the rate of straining decreases, this may be accepted as a convenient way of expressing the observed facts. Jeffries, however, attributed the phenomena under consideration to a difference between amorphous and crystalline metal. He assumed that the crystals are separated by amorphous films which are stronger than the crystals at atmospheric temperature but lose strength more rapidly on heating. The true explanation of the effect of time and temperature on fracture is however not quite so simple as this.

In short-time tensile tests at atmospheric temperature fracture occurs when the metal is strain-hardened to such an extent that the resistance

to deformation exceeds the resistance to fracture under the imposed conditions. During the deformation changes are produced in the crystal structure and these may have some influence on the magnitude of the breaking stress, but we are at present unable to investigate this, and strain-hardening is clearly the controlling factor, for the amount of deformation that precedes fracture increases as the rate of strain-hardening decreases. In the absence of strain-ageing, raising the temperature of testing decreases the rate of strain-hardening and therefore increases the amount of deformation that takes place before fracture. When strain-ageing occurs, however, raising the temperature of testing accelerates the strain-ageing and reduces the amount of deformation that precedes fracture. A further rise in the temperature results in recrystallization, and this increases the amount of deformation that precedes fracture. At temperatures at which strain-ageing is the predominant change, prolonging the time of testing should further decrease the amount of deformation that precedes fracture, whereas when recrystallization is the predominant change prolonging the time of testing should increase the amount of deformation that precedes fracture. These are the normal relations between time, temperature, deformation, and fracture. As the time and temperature of testing is increased, however, there is a tendency for these relations to be departed from, and it is frequently observed that even in the absence of strain-ageing the reduction in area at the point of fracture decreases as the time of testing is prolonged or the temperature of testing increased. This phenomenon is abnormal in the sense that it differs from what is most frequently observed, but it is nevertheless in accordance with what might be expected from consideration of the mechanism of deformation.

It may be noted in the first place that abnormal failure is facilitated by raising the temperature or increasing the time of testing. In each particular metal it occurs under conditions of stress, time, and temperature which permit recrystallization, and it is due to rupture of the cohesion at the crystal boundaries. Now we have seen that normal fracture occurs after a certain amount of strain-hardening, which causes the metal to resist without deforming the stress required to break it. Recrystallization of any of the three types mentioned above eliminates strain-hardening, and if the rate of recrystallization is sufficiently rapid in relation to the rate of deformation, no appreciable amount of strain-hardening may be produced. Under these conditions a specimen stressed in tension should draw down to a fine point before it fractures, i.e. the metal does not become sufficiently strain-hardened to resist without deforming the stress required to break it across an appreciable section. When recrystallization is less rapid than this, it does not counteract strain-hardening to such a great extent, but it does make it necessary to increase the amount of deformation in order to produce a given amount of strain-hardening. Thus the reduction in area at the

point of fracture increases as the rate of recrystallization increases and decreases as the rate of deformation increases. This is the normal effect of recrystallization. From this point of view it tends to prevent the crystals being brought into the condition necessary for fracture. At the same time, however, it has a pronounced effect on the crystal boundaries. Thus, as will be explained later, a characteristic feature of simultaneous deformation and recrystallization is that new crystals are continually appearing, growing, and replacing those previously existing, and as a result the crystal boundaries are always changing. As a result of this mobility of the boundaries it is not surprising that they adjust themselves under the action of the stress so as to permit extension of the specimen. In the course of the adjustment cohesion at the moving boundaries is easily ruptured and intercrystalline fracture initiated. Thus we may conclude that abnormal intercrystalline failure is liable to occur when the conditions of stress, time, and temperature permit recrystallization to proceed to such an extent that the strain-hardening which is necessary preliminary to transcrystalline failure is prevented, while rupture of the cohesion at mobile boundaries is facilitated.

THE MECHANISM OF THE CHANGES THAT FOLLOW DEFORMATION

The changes in crystal structure produced by deformation are irreversible, and although the application of force in the opposite direction may restore the original shape of a deformed metal it does not reproduce the original crystal structure, but actually causes a further change. These changes are not permanent, however, and are followed by others that tend to restore the metal to its original condition. The rate at which these subsequent changes proceed depends on the metal, the temperature, and the amount of deformation, and their most important effects are the alterations in mechanical properties that accompany them. In general, under suitable conditions of time and temperature, they cause the elimination of strain-hardening and this is referred to as recrystallization. In many cases, however, this elimination of strain-hardening does not take place directly by a progressive decrease in resistance to deformation, but is preceded by an actual increase. It is not certain whether this increase in resistance to deformation is a definite stage of recrystallization. Accordingly it is distinguished as strain-ageing. The previous sections of this chapter have been concerned with the effects of recrystallization and strain-ageing on the relations between stress, strain, time, and temperature. It is now necessary to consider their mechanism.

Strain-ageing.

The hump on the tensile strength-rate of loading curve (Fig. 72) and on the tensile strength-temperature curve (Fig. 80) is due to strain-

ageing, and the increase in resistance to deformation obtained by heating a deformed metal (Figs. 75 and 76) is also attributable to this phenomenon. It is most pronounced in iron and steel, and experimental study of the subject has been almost entirely confined to this group of metals. As shown in previous sections, it also occurs in other metals and may in fact be quite general, though it is frequently of extremely small magnitude. Discussion of its mechanism will be confined to iron and steel.

Strain-ageing means the increase in resistance to deformation (or in the rate of strain-hardening) that takes place with time after deformation, and results in an increase in hardness and tensile strength and a decrease in reduction in area. In iron and steel this change takes place slowly at atmospheric temperature and more rapidly as the temperature is raised. So far as its effects, and the conditions under which it takes place, are concerned, strain-ageing closely resembles another phenomenon known as precipitation-hardening. This takes place in many alloys, but cannot occur in pure metals. It is fully considered in Chapter VI, but its main features will be mentioned here, and in order to facilitate description a particular alloy will be considered, viz. one containing 96 per cent. of aluminium and 4 per cent. of copper. This alloy solidifies over a range of temperature, but at 565°C . solidification is complete and all the copper is incorporated in the aluminium crystals, forming what is known as a primary solid solution. During cooling from this point no change takes place in the alloy until 500°C . is reached and then, if the cooling is slow, the copper begins to be rejected from solution. It diffuses to the crystal boundaries and there forms crystals of a constituent containing both copper and aluminium known as CuAl_2 . By the time the alloy has reached 200°C . all the copper (except 0.5 per cent. which remains permanently dissolved in the aluminium crystals) exists as CuAl_2 forming envelopes round the aluminium crystals. When distributed in this way it has only a small effect on the mechanical properties of the aluminium. If, however, the alloy is cooled rapidly from 520°C . by immersion in water, the precipitation of copper from solid solution is prevented, and the alloy is retained at atmospheric temperature in the same condition as normally exists between 565° and 500°C ., i.e. with all copper atoms in solution in the aluminium crystals. In this condition, however, the alloy is not stable and changes slowly at atmospheric temperature. During this change CuAl_2 is precipitated in very minute particles throughout the aluminium crystals, and when distributed in this way has a pronounced effect in increasing their resistance to deformation. Thus, after rapid cooling, this alloy hardens with time at atmospheric temperature and the rate of hardening may be increased by heating.

After rapid cooling the alloy described above undergoes the same kind of changes as occur in iron and steel after deformation and the view is widely held that the ultimate cause of the increase in resistance to

deformation is the same in both cases. There is strong evidence for this view in that strain-ageing appears either to depend on, or at least to be greatly influenced by the presence of carbon, oxygen, or nitrogen. It is probable that small amounts of these elements may remain permanently dissolved in undeformed iron, and be rejected from solution in deformed iron, thus giving rise to conditions similar to those produced in the precipitation-hardening of rapidly cooled alloys. Similar behaviour on the part of other impurities may likewise be responsible for the strain-ageing of other metals. In the case of precipitation-hardening following rapid cooling, we are dealing with a change that might be expected to occur, for we know that such cooling prevents CuAl_2 being precipitated at a high temperature, and it is not difficult to infer that this suppressed precipitation may take place slowly at a low temperature. In the case of strain-ageing, however, if we are to regard it as an example of precipitation-hardening, we must admit that the constituents that give rise to it may remain in solution during very slow cooling from high temperatures and yet precipitate rapidly at low temperatures after deformation. Precipitation-hardening after accelerated cooling is fully discussed in Chapter VI, and strain-ageing, which appears to be a similar phenomenon occurring under different conditions, is considered in Chapter XII. Meanwhile, we may accept the precipitation hypothesis as the explanation of strain-ageing.

Recrystallization.

The changes in crystal structure produced by deformation tend to be eliminated under suitable conditions of time and temperature. As the most important effect of these is strain-hardening, the elimination of the changes is usually associated with the disappearance of strain-hardening. In many cases the first stage in the process that leads to the disappearance of strain-hardening is an increase in resistance to deformation due to strain-ageing, but whether this occurs or not, deformation is ultimately followed by the gradual disappearance of its effects. This is known as recrystallization.

Three types of recrystallization may be distinguished: (1) the recovery of the deformed crystals without the formation of new ones, (2) the formation of a system of new sub-crystals within each of the deformed ones, and (3) the replacement of the original crystals by a new generation the boundaries of which are not related to the original ones. Recrystallization of the first type results in a reduction in strain-hardening without a change in the microstructure. In all cases of heating after deformation this type of recrystallization proceeds to some extent and leads to a decrease in hardness before recrystallization of the third type begins. In each metal a certain temperature must be exceeded before new crystals can form, and the longer the metal is heated below this temperature the greater is the extent to which the first type of recrystallization proceeds. It has been shown in several investigations that substantial

reductions in strain-hardening can be produced in this way, and according to Tammann (71) it is possible to render hard material partially or completely soft without substantially affecting its structure. This type of recrystallization is not important in so far as heating metals after deformation is concerned, but it has a pronounced effect on their behaviour under prolonged stressing when the conditions of time and



FIG. 91. Showing sub-recrystallization in a specimen of carbonyl iron subjected to a short-time tensile test at 650° C. $\times 500$ enlarged $1\frac{1}{4}$ times (Jenkins & Mellor).

temperature permit it to proceed. The same applies to the second type of recrystallization which Jenkins and Mellor (70) observed in specimens subjected to long-duration tests at high temperatures. In this a new generation of sub-crystals appears in some or all of the deformed crystals, giving rise to structures like that shown in Fig. 91. It is doubtful whether this takes place when metals are heated after deformation at ordinary temperatures, but it appears to be of common occurrence in metals subjected to prolonged stressing at elevated temperatures.

The third type of recrystallization is the most important and is generally implied when recrystallization is used in a structural as distinct from a mechanical sense. It affects the behaviour of metals under prolonged stress and is furthermore of great importance in connexion

with mechanical working operations. When mechanical shaping operations are carried out at low temperatures, strain hardening occurs, and if it proceeds far enough, the metal may be rendered unsuitable for further shaping or for service. When it is necessary to soften strain-hardened metals, they are heated to a temperature at which recrystallization of the third type can proceed rapidly. This is known as annealing. When, however, it is necessary to produce large changes in shape or to deform large masses, mechanical-working must be performed while the metal is hot so as to take advantage of its greater plasticity and freedom from strain-hardening. Hot-working, as this is called, is most conveniently carried out in a range of temperature in which recrystallization proceeds concurrently with deformation. In the case of iron, nickel, copper, and aluminium the cold-working and hot-working ranges are quite distinct, and are separated by a range in which the metals may be used in service if account is taken of the effects of prolonged loading. Thus for these metals the range of temperature above atmospheric may be divided into three parts, viz. the cold-working, creep, and hot-working ranges respectively. Owing to the practical importance of the third type of recrystallization it will now be considered in some detail in connexion with certain other phenomena associated with it.

The Stability of Undeformed

The crystals formed when a metal solidifies do not change very much in size and shape unless the metal undergoes constitutional changes or is deformed. This does not mean that each of the crystals constituting the metal is in a state of equilibrium. Each individual crystal has actually a tendency to grow at the expense of its neighbours, and to assume an external shape approximating as closely as possible to that of a sphere as is consistent with the fact that the aggregate of crystals must fill space. The condition of relative equilibrium existing in the metal is simply the result of a balance between the tendencies possessed by the separate crystals. The individual crystals in an aggregate can never attain a condition of true equilibrium, so that we cannot in general define the stability of a crystal as a state in which it exhibits no tendency to change its size or shape. Stability in this connexion must rather be defined as the capacity to resist absorption by other crystals, and therefore implies the capacity to absorb them. When all the crystals in an aggregate are equally stable in this sense of the term, the aggregate is in equilibrium.

The stability of a crystal increases with its size, so that larger crystals tend to absorb smaller ones. For this to take place, however, there must be a certain mobility of the atoms, and for this reason the rate of absorption increases with temperature. If an aggregate of small crystals of about the same size is produced at a low temperature and heated, the crystals will grow to a certain limiting size, which is greater and is reached in less time the higher the heating temperature. Whether this would happen if the original small crystals were all exactly of the same

size and shape is another matter. It is sufficient to state that in aggregates of small crystals, such as are actually produced at low temperatures, these changes take place. To explain them it must be inferred that, as the temperature is raised, crystals of a given size become unstable, and that the amount of difference in size and shape required to enable one crystal to grow at the expense of another decreases. Therefore, in a given metal a certain minimum crystal size is stable at a given temperature, and if the actual crystal size is less than this, some of the crystals will grow at the expense of their neighbours until the equilibrium size is attained.

When a metal is solidifying, and just after solidification is complete, the crystals have the opportunity to attain a size and shape that is about the same for each crystal and is stable at that temperature, and consequently at all lower temperatures. As metals cannot be heated above the melting-point without melting, the crystals formed on solidification are stable unless the metal undergoes constitutional changes or is plastically deformed. The case is different with metals deposited electrolytically from solution, for here the crystals are formed at low temperatures and therefore tend to increase in size when the temperature is raised.

The Recrystallization Temperature.

Once a metal has been plastically deformed it possesses a tendency to revert to its original state of stability by the formation of new crystals, and this is greater the larger the amount of deformation and the lower the temperature at which it is performed. The changes that arise from it proceed at a rate that depends on the temperature at which the metal is maintained or to which it is heated. A definite stage in these changes is that marked by the first appearance under a high-power microscope of new equiaxed crystals growing in the elongated crystals produced by deformation. This represents neither the beginning nor the end of these changes, but is a convenient point in the progressive change to use as a means of comparing the effect of different amounts of deformation, &c. Another definite stage is reached when all the original deformed crystals have been absorbed by the new generation. This is also rather difficult to ascertain, and recrystallization is usually studied by following the elimination of strain-hardening by means of tensile or hardness tests.

The phenomenon of recrystallization has been mainly studied in connexion with metals deformed at ordinary temperatures and subsequently heated, for its most obvious practical significance is in relation to the softening of metals that have been hardened during cold-rolling, -drawing, or -pressing. In these operations, which are regularly performed at ordinary temperature, the metal becomes hardened, and a point is reached at which further attempts to deform it result in fracture. In order to facilitate further deformation, and sometimes in order to put the metal into a suitable condition for service, it must be softened by permitting it to recrystallize. In all ordinary cold-working operations the

metal is severely deformed before it is softened, and therefore the conditions required for recrystallization after such work are of considerable importance. The most important factor in promoting recrystallization is temperature, and although the process is affected by time and a number of other factors, it is customary to speak of the recrystallization temperature of a metal. The recrystallization temperatures of a number of severely deformed metals are given in Table 23. These have been determined by observing the first appearance of new crystals by means of a microscope. With longer periods of heating new crystals would appear at lower temperatures, and in slightly deformed metals they would not appear until higher temperatures, but the figures shown indicate the temperatures below which recrystallization is slow and above which it is rapid. In some of the metals, e.g., lead, tin, zinc, and cadmium, the recrystallization temperature is either at or below atmospheric temperatures, and this has an intimate bearing on their mechanical properties. Another factor that has a pronounced effect on recrystallization is purity, and small quantities of impurities raise to a marked extent the temperature at which recrystallization begins after a given amount of deformation. This is further discussed below and in relation to various metals in Chapters XV and XVI. Meanwhile, it may be noted that the figures given in Table 23 refer to metals of commercial purity and have little bearing on the behaviour of metals of very high purity. Furthermore, these figures indicate the temperatures at which recrystallization begins and not those at which it is completed in a relatively short time.

TABLE 23

Recrystallization Temperatures (17)

<i>Metal</i>	<i>Approximate lowest recrystallization temperature ° C.</i>	<i>Metal</i>	<i>Approximate lowest recrystallization temperature ° C.</i>
Iron	450	Tantalum	1,000
Nickel	600	Tungsten	1,200
Gold	200	Molybdenum	900
Silver	200	Zinc	Room temperature
Copper	200	Lead	Below room temperature
Aluminium	150	Tin	Below room temperature
Platinum	450	Cadmium	About room temperature
Magnesium	150		

The significance of the recrystallization temperature depends in the first place on the metal being severely deformed, and in the second on the hyperbolic form of the curve connecting time and temperature, so that the change proceeds slowly below a certain narrow range of temperature and rapidly above it. In general, however, the recrystallization temperature is progressively lowered as the amount of deformation is increased and as the accuracy of the methods of detecting the change is improved. A very small amount of deformation may produce a tendency

to recrystallize that does not take effect at any temperature below the melting-point. As the amount of deformation is increased, the metal begins to recrystallize below the melting-point, and at progressively lower temperatures as the deformation is further increased. In promoting recrystallization a few minutes at 300° C. may be as effective as a few weeks at 200° C. or many years at atmospheric temperature. Yet, although the changes at atmospheric temperature may be slow, and although new crystals may not appear in any finite time at this temperature, the metal is unstable, and undergoes changes which may be detected in other ways.

Nuclei.

In all phenomena connected with crystallization or recrystallization the conception of nuclei is important. Frequently, in the crystallization of liquid metals or of salts from solutions, particles of extraneous material serve as nuclei on which the crystals grow, but in its broadest sense the term does not necessarily imply particles of extraneous material. It is commonly used to describe crystals at the very beginning of their growth when they consist of a few atoms united to form an element of the space-lattice. In this sense a nucleus is just a small crystal, but the term is also used with reference not to these, but to the point at which they will immediately appear. When the term is used in this way a nucleus is simply an abstraction, but it is a convenient meaning to attach to it. When a liquid metal is approaching its freezing-point, any point in it may be regarded as a nucleus. At the appropriate instant a number of crystals begin to form at certain of these points, the distribution of which is governed by the laws of probability. If the temperature of the metal continues to fall, more new crystals appear, while those originally formed increase in size. Rapid abstraction of heat from the metal favours the formation of new crystals, while slow abstraction favours the growth of existing crystals. When, in the course of solidification, crystals of different sizes come into contact, the larger crystals tend to absorb the smaller.

A plastically deformed metal about to recrystallize does not provide the same conditions for the appearance of new crystals as a liquid metal about to solidify. In the latter there is, at any point in the mass, an equal probability that a crystal will begin to form. In the former the probability that a new crystal will appear at a given point depends upon the amount of strain existing there. It was shown in the description of deformation that this involves relative movement of the constituent parts of the crystals along certain planes, and in crystals thus deformed the strain is greatest at those points where slip has actually occurred. When deformation has been severe and slip has taken place along a large number of planes, the conditions in a deformed metal approximate to those in a liquid metal as far as the existence of nuclei for the formation of new crystals is concerned. But when the crystal has been deformed

only slightly, there are certain points where the probability that a new crystal will appear is greater than at others. In a given piece of metal the amount of slip that takes place varies slightly from crystal to crystal, and the greatest degree of strain appears to be produced at the boundaries of the crystals. After a given amount of deformation has been applied to an aggregate, the degree of strain produced varies from point to point, so that, when it is heated to enable recrystallization to take place, new crystals first appear at certain points on the boundaries and slip planes of certain crystals.

The Size of Crystals formed by Recrystallization.

If a metal is deformed and then heated, the temperature at which recrystallization begins depends on the degree of deformation. If it is not heated sufficiently, no recrystallization will take place. If it is heated to the lowest temperature at which recrystallization can begin, then new crystals will appear at the points of greatest strain. If this temperature is correctly adjusted, the number of points at which new crystals appear is very small. The new crystals have a greater stability than the deformed crystals around them, for although the degree of strain varies from point to point, the mass of deformed material as a whole is less stable than the new and undeformed crystals. If sufficient time is allowed, the new crystals will absorb all the deformed metal.

If the temperature is not held constant at the point where new crystals first appear but is raised progressively, more and more new crystals will begin to form at points where the original strain was less. At any given instant during heating the new crystals will not be of exactly the same size. Those that first appeared will be slightly larger, but if the temperature is held constant at any point, growth and absorption will proceed until a condition of equilibrium is reached. This will be reached in less time, and the resulting crystal size will be greater, the higher the temperature of heating.

If the two operations described above are combined, i.e., if the deformed metal is first heated at the temperature at which new crystals appear at the points of greatest strain, and is then heated to higher temperatures, very large crystals may be produced. During heating at the first temperature a few new crystals begin to grow and these attain an appreciable size. When the temperature is raised, more new crystals appear, but they are always much smaller than the original new crystals and are soon absorbed by them. As the amount of difference in size that is required to enable one crystal to grow at the expense of another decreases with rising temperature, a point is eventually reached at which even the first formed crystals are able to absorb one another. In this way, under the appropriate conditions, fairly large masses of metal may be converted into one crystal.

In practice, as already stated, metals are usually reheated after severe deformation, and as the object of this is to bring about rapid recrystal-

lization, the heating is carried out at temperatures high enough to permit this to begin at many points. The crystal size produced in this way depends entirely on the time and temperature of heating. But when parts of the metal have been subjected to considerably less deformation than the remainder, the crystal size is affected by the other factors described above, and some very interesting results have been obtained under these conditions. A few of these may be described in order to illustrate the operation of the factors that control recrystallization and grain growth.

In 1914 Chappell (72) described the results of experiments on the recrystallization of deformed iron. In some of these, tapered bars were fractured in a tensile testing machine, and a regular variation in strain

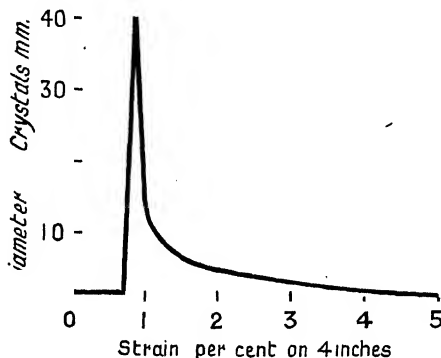


FIG. 92. Effect of the amount of previous strain on the crystal size produced in six hours' heating at 800° C. (copper).

thus obtained between their smallest section, where fracture occurred, and their greatest section, where the stress did not exceed the yield-point. The bars were then heated at various temperatures. At 600° C. recrystallization began in the most highly deformed metal near the point of fracture. Small crystals were formed at first and increased in size as the temperature was raised. At the same time recrystallization extended farther from the point of fracture, and at 870° C. had almost reached that portion of the bar where the yield-point was just exceeded during the original stressing. The size of the new crystals increased progressively with the distance from the point of fracture, and at the boundary of the region of recrystallization there was a sudden decrease in crystal size, from that of the large crystals formed by recrystallization to that of the original crystals that had not been sufficiently strained to recrystallize at the temperature in question.

Carpenter and Tamura (73) performed a number of experiments which further illustrate the phenomena described above. Specimens of copper were subjected to different amounts of deformation and heated for six hours at 800° C. Their results are shown in Fig. 92. At 800° C. no recrystallization occurred following on an elongation of less than 0.8 per cent. On heating, after an elongation of 0.8 per cent., very large

TIME, TEMPERATURE, AND DEFORMATION

were produced, and as the amount of deformation was increased, the size of the crystals decreased, at first rapidly and then more slowly. Similar results were obtained by Carpenter and Elam (74) and by Seligman and Williams (75) with aluminium.

The above experiments illustrate the effect of varying the deformation and keeping the temperature of heating constant. Under these conditions, on the one hand, a large number of small crystals is produced in the most highly deformed material because the number of nuclei is large, and because it is heated well into the range of recrystallization. Large crystals, on the other hand, are produced in that material which is just sufficiently deformed to enable recrystallization to begin at a few points. If heating is to be performed at a constant temperature, there is therefore a critical degree of deformation that will produce very large crystals. If, however, the amount of deformation is constant, there is a critical temperature at which large crystals will be produced. To obtain this the deformation must be slight, otherwise the temperature at which fairly large crystals might be obtained would be too low to admit of their growth.

It was by taking advantage of the conditions under which large crystals can be produced by deformation and heating that Carpenter and Elam (31) succeeded in converting ordinary aluminium test-bars containing a large number of crystals into one crystal. The same method was subsequently used by Edwards and Pfeil (32) to obtain large single crystals of iron. In order to do this it is necessary to adjust the deformation and temperature of heating so that *recrystallization begins and proceeds to some extent at one point only*. It does not matter whether or not crystallization subsequently begins at other points, for as long as these crystals do not become equal in size to the original one they will eventually be absorbed by it. Besides the factors mentioned there are others which affect the production of large crystals under controlled conditions. The size of the crystals before deformation is one of these, for the size of the crystals in an aggregate affects the conditions produced in it by a given amount of deformation. Slight variations in the purity of the metal also influence the process, particularly if the impurities occur as distinct particles, and Jeffries and Archer (17) consider that such impurities must be regarded as controlling factors in this respect. These authors describe experiments which indicate that under certain conditions the presence of a critical amount of obstructing material, in the form of impurities not held in solid solution by the metal, is necessary for the production of large grains.

When recrystallization is considered generally it is seen to be a most complicated phenomenon. The actual process depends in the first place on the number of nuclei at which recrystallization begins, in the second place on the rate at which crystals growing from these nuclei absorb the strained crystals surrounding them, and finally on the extent to which the crystals resulting from recrystallization are capable of

absorbing one another. Each of these factors is affected by the original amount of deformation and the temperature and time of heating, and the effect of this last factor may be further complicated by varying the rate of heating, or by heating at one temperature and then at another. In general, however, the number of nuclei increases with the amount of deformation and so does the tendency to recrystallize. Thus a drastically deformed sample will recrystallize at a lower temperature than a lightly deformed one, and as the change will begin at a greater number of points more crystals will be formed. After recrystallization is completed, prolonging the time or raising the temperature of heating will enable some of the newly formed crystals to absorb their neighbours, but this is a slower process than the absorption of deformed crystals. It means, however, that after recrystallization is completed the crystal size increases with the time and temperature of heating.

The Effect of Impurities.

The time and temperature at which recrystallization begins after a given amount of deformation is greatly affected by the presence of impurities. In a given metal different impurities produce effects of varying magnitude, and numerous specific instances are considered in Part VI. For the time being it is sufficient to state that impurities generally raise the range of recrystallization, that small amounts produce large effects, while further increase in the amounts present results in less pronounced alteration in the recrystallization range. So marked is the effect of small quantities of impurities that observation of the recrystallization temperature is used as a means of determining purity. As an example of the effects of impurities on recrystallization some experiments performed by Calvet (593) may be described. This investigator used six samples of high-purity aluminium varying in purity from 99.9986 to 99.96 per cent. of aluminium. Each sample was subjected to the same amount of cold-working i.e. a reduction in thickness from 20.4 mm. to 1.5 mm. by ten cold-rolling passes. Specimens from each sample were then heated at various temperatures for different times, and the progress of recrystallization followed by measuring the decrease in tensile strength and the increase in elongation. Softening of the purest sample (99.9986 per cent. Al) was completed in 6 to 10 minutes at 100° C. and even at 16° C. softening was comparatively rapid. The next sample (99.997 per cent. Al) was not completely softened after 6 hours at 100° C. and when the purity was reduced to 99.996 per cent. only a small amount of softening occurred in 240 hours at 100° C. The complete annealing of this sample required 48 hours at 175° C. When the purity was decreased to 99.99 per cent. softening was almost completed in one hour at 225° C. To produce a similar result in metal of 99.98 per cent. purity, 24 hours at this temperature was required, while the sample containing 99.96 per cent. of aluminium was incompletely softened after 100 hours.

Impurities that exist in the solid metal as distinct particles of the type known as 'inclusions' may have further effects on recrystallization. Such inclusions tend to concentrate at the boundaries of the crystals formed at solidification. When the metal is deformed these tend to be drawn into sheets or rows parallel to the direction of rolling or drawing. When recrystallization occurs the new crystals are to some extent prevented from growing across these sheets and therefore tend to adopt an elongated form as described in Chapter XII in connexion with 'banding' in steel and in Chapter XVI in connexion with the recrystallization of



Recrystallized brass. $\times 100$. (Cook and Miller.)
(*Journal of the Institute of Metals.*)

aluminium. Even when they do not lead to the formation of elongated crystals inclusions tend to retard grain growth and are intentionally produced in tungsten for this reason.

Preferred Orientation and Twins.

The preferred orientations produced when polycrystalline metals are deformed tend to persist to some extent even after recrystallization. Thus when a metal is deformed to such an extent that a preferred orientation is developed, the promotion of recrystallization by annealing does not result in a random orientation of the crystals. The preferred orientation persisting after annealing is usually different from that produced by the deformation, but it is of the same type.

In discussing twinning in Chapter III it was pointed out that twinned crystals are not observed in cast metals and that their formation is plainly due to deformation. Twinned crystals are frequently observed in deformed metals, but they are very conspicuous features of recrystallized metals. Thus when any of the face-centred cubic metals (except aluminium), or any of the hexagonal metals, are deformed at room temperature and annealed, or deformed at high temperatures

when recrystallization accompanies deformation, twinned crystals are obtained. These twinned crystals can be detected in the early stages of recrystallization and observed to grow with the other crystals, and it appears that they originate from twins produced during the deformation. Twinned portions of a given crystal are divided by the composition planes, and thus the boundaries between twins are straight and sharp and quite different from those between crystals. In Fig. 93, which represents recrystallized brass, many twins are shown, and the appearance of such a structure is evidence of deformation followed by recrystallization. It may be produced either by deformation at atmospheric temperature followed by heating or by deformation at high temperatures in which concurrent recrystallization occurs.

PART II

ALLOYS

CHAPTER V

THE SOLIDIFICATION OF METALS AND THE STRUCTURE AND CONSTITUTION OF ALLOYS

ALLOYS

IN Chapter I it was explained that an alloy in the scientific sense of the term is any metallic substance other than a pure metal, while in a practical sense it is a mixture of metals intentionally prepared to secure certain desirable properties. In this part of the book we shall deal with alloys in the former sense and shall in general be concerned with the solidification, crystal structure, microstructure, and constitution of metallic substances containing more than one element. This covers all such substances at present known, and in an alloy so defined it is theoretically possible for any number of elements to be present in any proportions and to owe their presence to a variety of reasons.

In nearly all alloys one metal predominates. This is the basis metal. If the alloy has resulted from attempts to prepare a pure metal, the total of the other elements is small, as, e.g., in carbonyl iron which contains about 0.015 per cent. carbon, 0.002 per cent. silicon, 0.0005 per cent. sulphur, 0.0008 per cent. phosphorus, 0.005 per cent. manganese, 0.011 per cent. nickel, 0.002 per cent. copper, 0.016 per cent. oxygen, and 0.003 per cent. nitrogen, making a total of 0.0553 per cent.; or in high conductivity copper which contains about 0.0018 per cent. silver, 0.001 per cent. lead, 0.0009 per cent. antimony, 0.0026 per cent. tellurium, 0.0035 per cent. iron, 0.0028 per cent. nickel, 0.0026 per cent. sulphur, and 0.0315 per cent. oxygen, making a total of 0.0467 per cent. As the precautions taken to ensure a high degree of purity are relaxed the proportions of the other elements increase, as, e.g., in Armco iron which contains about 0.236 per cent., in casting copper which contains about 0.6 per cent., and in commercial aluminium which contains about 1 per cent. of them. In such alloys the elements present in the basis metal are known as impurities and they are there either because it is technically impossible to eliminate them or because the advantages that would follow from their removal are not considered to warrant the expense involved. Other alloys, however, contain elements that are added by design or allowed to remain because they produce certain desirable properties. These elements are known as additions and may be present in large amounts as e.g. in Monel Metal where 30 per cent. of copper is added to nickel, in brass where from 30 to 40 per cent. of zinc is added to copper, or in

certain types of stainless steel where 30 per cent. of chromium is added to iron. They may also be present in large numbers as, e.g., in certain heat-resisting steels which contain chromium, nickel, silicon, aluminium, tungsten, and molybdenum.

In general the elements which occur in a given alloy are (1) associated with the basis metal in the ore and not subsequently eliminated, (2) picked up during the manufacturing operations, (3) added to eliminate or counteract the effect of another element, (4) added to produce certain desirable properties, or (5) are present as impurities in the additions made under (4). If special efforts are made to detect every element present in a given sample, it will generally be found to contain a comparatively large number. Thus, in the analysis of carbonyl iron given above, nine elements are mentioned, but by spectrographic analysis traces of four others, viz. calcium, aluminium, magnesium, and silicon, were found (70). Yet in this case a metal of high purity is concerned, and in commercial alloys to which several additions, each containing impurities, have been made, and in which no exceptional precautions have been taken to prevent the presence of small quantities of other elements, a very large number of these may be detected if all the refinements of modern analysis are brought into use. It is not customary, however, to do this except when investigating the properties of metals of the highest available purity and as a rule only those elements present in 'effective' proportions are determined by analysis.

Apart from accidental impurities the elements intentionally present may originate in several different ways. The carbon and silicon which are essential components of the alloy known as cast iron are picked up by the iron during the reduction of iron oxide in the blast-furnace. Thus cast iron is the product of the first stage in the manufacture of iron. Wrought iron and steel are made by purifying cast iron. Originally brass, bronze, and nickel silver were made by smelting mixed ores containing the various component metals, but to-day these, like nearly all other non-ferrous alloys, are made by mixing the component metals. In this method the basis metal is first melted and the others are subsequently added in the requisite proportions. Sometimes they are added as virgin metals as, e.g., zinc or tin to make brass or bronze from copper, but in many cases it is found advisable to prepare what are known as intermediate alloys and to use these in manufacturing the alloys required. Thus the various additions made in the manufacture of alloy steels are, e.g., ferro-chromium, ferro-tungsten, ferro-vanadium, &c., and a similar procedure can be followed in making non-ferrous alloys. Several methods are available for making alloys from solid metals. Steel was originally made by heating wrought iron (which contains hardly any carbon) with some carbonaceous substance so as to cause carbon to diffuse into it. This was a lengthy operation and has been almost completely superseded as a method of making steel. It is still employed extensively, however, in the process of case-hardening in order to increase the carbon content at

the surface of steel articles. Recent advances in the preparation of metal powders have opened a way for the production of alloys by mixing and compressing powders and then heating them. Hard carbide cutting tools and porous bearing metals are made in this way, and further extension of this method will no doubt follow. In general, however, alloys are first prepared in a molten condition and may be said to be made when a melt of the requisite composition has been produced.

Liquid Alloys.

Little is known about the mechanism of the solution of molten metals in one another, and all that can be said at present is that when this occurs the result is a homogeneous mixture of their atoms. It is not known why certain metals dissolve in each other in all proportions when molten while others do not. Certain pairs of liquids such as water and alcohol dissolve in each other in all proportions, forming homogeneous solutions. They are said to be completely miscible, and many pairs of metals are similarly related. Other liquids, like water and phenol or water and ether only form solutions within certain limits, while water and oil or water and mercury do not dissolve in each other at all. Similar phenomena are exhibited by liquid metals, and the different systems may be classified as Completely Miscible, Partially Miscible, or Immiscible.

When completely miscible liquids are mixed together, a single homogeneous solution results, whereas when partially miscible liquids are mixed two solutions are formed. At atmospheric temperature water can dissolve 9 per cent. of phenol, and phenol can dissolve 27 per cent. of water. If these liquids are mixed in any proportions not within these limits a single homogeneous solution is not obtained. If, e.g., equal quantities of water and phenol are mixed they form two layers of the saturated solutions. If an additional quantity of either liquid is added no change takes place in the composition of the solutions, but their relative proportions are altered. If the temperature is raised, however, the mutual solubilities of the two liquids are increased, and at 68.4° C. water dissolves 36 per cent. of phenol and phenol dissolves 64 per cent. of water. The two solutions are therefore continuous and above this temperature a single homogeneous solution results from the mixture of the liquids in any proportions. This is known as the 'critical solution temperature'. Other pairs of partially miscible liquids show similar behaviour. Various degrees of miscibility are observed in alloys. Strictly speaking, complete immiscibility can hardly be said to exist between liquid metals, but in certain cases the reciprocal solubility of the components is so small as to be undeterminable by present known methods. Such substances when mixed together separate into two distinct layers, each of which is practically pure. The mutual solubility of partially miscible metals increases with temperature, but in all cases so far investigated the critical solution temperature lies above the boiling-point of one of the metals and cannot be determined. In the study of alloys,

however, it is the mutual solubility at temperatures just above the melting-point that is important and alloys are classified according to their reciprocal solubilities in this range. Most of the best known alloy systems are derived from metals that are completely miscible in the liquid state, but this is by no means universal, and a list of forty pairs of metals that exhibit various degrees of partial miscibility, which in some cases is one of practical immiscibility, is given by Desch (7). Among the pairs of common metals that belong to this class aluminium and lead, and copper and lead, may be mentioned. The first pair is almost immiscible at a temperature just above the melting-point of aluminium, whereas copper dissolves 38 per cent. of lead and lead 7.5 per cent. of copper at a temperature just above the melting-point of copper.

When immiscible metals are mixed in any proportions, or when partially miscible metals are mixed in proportions that do not fall within the limits of mutual solubility, two layers of liquid are formed and a homogeneous solid alloy cannot result on freezing. If, however, the molten alloy is vigorously stirred, the two layers may be made to mix, and if the two metals are not allowed to separate, this condition may be preserved in the solid alloy which then consists of globular particles of one metal distributed throughout a matrix of the other. This is the kind of structure obtained in nickel-silver alloys used for coinage.

Attention will be confined in the first place to alloys composed of metals that are completely miscible when molten. The melt consists of a solution or a mixture of the atoms of the component metals, but when solidification takes place the atoms sort themselves out and form various kinds of crystals which are the constituents of the alloy. The size and shape of these crystals and the way in which they are arranged with respect to each other constitute the structure of the alloy, and it is with the process of solidification and the constitution and structure of alloys that this chapter is concerned. But in many alloys, and particularly in the most important industrial alloys, changes which greatly alter the constitution and structure occur after solidification. These are considered in the next chapter.

THE SOLIDIFICATION OF PURE METALS

Before proceeding to deal with the solidification of alloys it is necessary to consider certain aspects of the solidification of pure metals. In practice this process is influenced to a great extent by what may be generally described as external conditions. Freezing takes place in a mould and the temperature of the metal is lowered by the abstraction of heat through it. As a consequence the metal in contact with the mould is always at a lower temperature than that farther from it and the resulting temperature gradient has a pronounced effect on the process of solidification. Furthermore, this usually begins and frequently

proceeds to a considerable extent before the turbulence caused by pouring the metal into the mould has subsided. The agitation caused by this, and by the evolution of gas from the metal, the mould wall, and the mould dressing also has a marked effect on solidification. So likewise have the innumerable small particles of non-metallic matter known as inclusions which are almost invariably present in the melt. All these factors are practically important and are considered in Chapter IX. We shall here consider solidification as it would take place in a mass of metal in which the temperature is uniform, in which there is no agitation, and in which inclusions are absent.

Nuclei and Undercooling.

Two aspects of solidification may be considered, namely, the formation of nuclei and crystal growth. Certain types of inclusions serve as nuclei for the growth of crystals but in general small crystals spontaneously form in the melt. At a temperature considerably above the freezing-point the atoms in a molten metal are in a state of continual movement and the forces of repulsion predominate. Although the atoms are constantly making contacts they exhibit no tendency to combine. As the temperature approaches the freezing-point the rapidity of movement of the atoms decreases and the forces of repulsion decrease relatively to those of attraction. The atoms therefore display an increasing tendency to combine together to form fragments of their characteristic space-lattice. At first, these have only a temporary existence, but as the temperature continues to fall their stability increases and they are formed in increasing numbers. Eventually certain of these minute crystals become sufficiently stable to resist the forces tending to disrupt them and begin to attach additional atoms. Crystallization proper has then begun.

The small fragments of space-lattice formed in the first instance are less stable and more easily disrupted than the larger fragments subsequently formed. Consequently, the temperature must be lowered to a greater extent to produce stable nuclei than is required for the subsequent attachment of additional atoms to them. From this arises the phenomenon of under-cooling. The true freezing-point is the highest temperature at which crystallization can proceed. Above this temperature the molten metal is stable and exhibits no tendency to solidify even when suitable nuclei are present. Whenever the melt is cooled below the true freezing-point it becomes metastable, and crystallization will begin if suitable nuclei are present. In their absence, however, it cannot take place, for the minute space-lattice fragments formed in this range are not sufficiently stable to act as nuclei for crystal growth. Under these conditions the melt must be further cooled until they acquire the requisite degree of stability. It then enters the labile range in which crystals begin to form spontaneously. If the melt is shaken, crystallization sets in as soon as the labile range is reached, but if it is still it may be cooled

for some distance into this range before crystals form. Molten metals cannot be cooled far into the labile range or maintained for a long time in it without solidifying, but other liquids can, and certain liquids of high viscosity normally cool to the ordinary temperature without crystallizing at all. Glasses and lavas are examples of these. Their viscosity at temperatures below their true freezing-point is so high that crystallization can only take place extremely slowly. If sufficient time is not allowed they do not crystallize, but their viscosity increases as the temperature falls and eventually attains a value equal to that of a solid. For this reason they are regarded as supercooled liquids rather than as true solids.

The effects of agitation and inoculation with suitable nuclei have been studied mainly in connexion with salt solutions and organic substances, but although the purely scientific aspects of the subject have not been extensively studied in metals, the practical consequences are known to be of importance. As already mentioned, agitation enters into nearly all casting operations and inoculation is of particular importance in connexion with aluminium-silicon alloys (Chapter XVI) and cast iron (Chapter XIV). It should further be stated that the rate of cooling of a melt has a pronounced effect on the phenomena which occur on solidification, and whereas slow cooling may produce similar effects to inoculation, rapid cooling tends to bring the melt into the labile range before crystallization begins. Disregarding for the time being the distinction between the metastable and labile ranges and the effects of agitation, inoculation, and rate of cooling, it may be said that owing to the relative instability of the nuclei first formed a metal must be cooled below its true freezing-point before crystallization begins. As, however, freezing is accompanied by an evolution of heat, the temperature of the metal tends to rise during solidification, and if the rate of abstraction of heat is sufficiently slow it will rise to the true freezing-point and solidification will then proceed at a constant temperature.

During cooling space-lattice fragments begin to form at a higher temperature than that at which they become capable of acting as effective nuclei. During heating a corresponding lag in the destruction of the crystal fragments is observed, and the forces of attraction that predominate in the solid are not entirely overcome until the metal is heated to a temperature somewhat higher than that at which it becomes almost completely molten. After the metal is melted groups of atoms remain in the geometrical arrangement characteristic of the crystals and these are gradually destroyed as the temperature is raised. If the metal is cooled again before this happens, they assist in the formation of the nuclei required for resolidification. Thus the temperature to which a molten metal is heated may have an effect on its behaviour during its resolidification. Some years ago this phenomenon was considered to be of great importance in the metallurgy of cast iron, but more recent views attribute the observed effects of superheating to the elimination of

non-metallic particles rather than to the destruction of fragments of graphite crystals (Chapter XIV).

The Distribution and Number of Nuclei.

When solidification is not influenced by temperature gradients arising from the method of cooling, all the crystals in the solid metal exhibit a marked similarity in size and shape. This is apparently the result of the interaction of several factors. It may be assumed that the fragments of space-lattice that first attain sufficient stability to serve as centres of crystallization will tend to be distributed at random. When crystallization begins at these, however, the heat evolved in the process produces temperature gradients such that the temperature of the melt is higher in the vicinity of crystals than elsewhere. Thus new nuclei will tend to form at other points rather than in their vicinity, and the continuation of this process will tend to bring about a uniform distribution of crystals. Furthermore, a nucleus is not a fixed point and a growing crystal is free to move. As they all grow at the same rate, they will all be about the same size at any instant before contacts are established between crystals growing from different nuclei. Since metal crystals are with few exceptions more dense than the melt from which they form, these contacts are first established while the crystals are slowly sinking. After this they will tend to push each other into those parts of the liquid where they are free to move and grow. Because of this the size of the different crystals will be affected by their rate of growth, which is the same for all, as well as by the distribution of the original nuclei.

The approximate similarity in the shape of the individual crystals in a solid metal arises from the fact that each crystal assumes the same shape while growing freely in the melt, and it is only towards the end of solidification when each becomes practically surrounded by others that the effects of mutual interference come into play and lead to various modifications of the shape that is assumed during unrestricted growth. The distribution of nuclei and the rate and mode of growth of the crystals are the factors that lead to the similarity in the size and shape of the crystals in a given sample of metal. The number of crystals in a given volume and consequently the average size of the crystals is, however, controlled by the number of nuclei. As the tendency for stable fragments of space-lattice to form increases with falling temperature, it follows that increasing numbers of nuclei will appear as the metal is cooled below its true freezing-point. Whenever crystallization sets in, heat is evolved, and the subsequent changes in temperature depend on the relations between the rate of evolution of heat and the rate of its abstraction. The more rapidly heat is abstracted from the melt, the further it will be cooled before the heat evolved in crystallization begins to produce a rise in temperature and the smaller will be this rise. Thus, rapid abstraction of heat (i.e. rapid cooling) causes crystallization to begin and continue at lower temperatures, while slow abstraction of heat

permits it to begin and continue at higher temperatures. Consequently, rapid cooling produces many nuclei, and a small average crystal size, while slow cooling produces fewer nuclei and a larger average crystal size.

The Growth of Metallic Crystals.

There is a marked difference in the mode of growth of metallic and non-metallic crystals respectively. When a crystal is growing in a super-saturated solution or an under-cooled molten mass of the same substance, the form it assumes during growth is determined by the different velocities of growth in different crystallographic directions. If the crystal is non-metallic the process is somewhat as follows: Assuming the nucleus to be a point, then if growth proceeded at the same rate in all directions the result would be a crystal of spherical shape. But the rate of growth is different in different crystallographic directions and after the nucleus has become a crystal of appreciable size its shape is determined by this. If, e.g., a crystal having the shape of a cube is to grow from a point, the rate of growth must be greatest in the directions of the corners and least in the directions of the centres of the faces. Furthermore, as every point on a given face lies at a different distance from the centre of the cube, the rate of growth must vary gradually with the direction so that faces will be formed and maintained. In other words every line that can be drawn from the centre of the cube to a point on its surface is a direction of growth. The lengths of these lines increase from a minimum in the case of the ones that meet the centres of the faces to a maximum in the case of those that meet the corners, and the rate of growth in the directions represented by these lines must be exactly proportional to their length. In non-metallic crystals the rate of growth in different directions varies gradually with the direction, and crystals with plane faces are produced. In metallic crystals, however, the rate of growth varies discontinuously with the direction, and dendritic or skeleton crystals result.

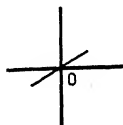


FIG. 94

In metals that crystallize in the cubic system growth takes place preferentially in the directions of the axes of this system, i.e. in three directions at right angles to each other. If point *O*, Fig. 94, is considered to represent the nucleus of a crystal, then if it is non-metallic a symmetrical crystal in the form of a cube or octahedron or some other shape will grow around it. If it is metallic, however, the first stage in growth will be the production of a six-branched skeleton as indicated by the lines in Fig. 94. These branches have an appreciable thickness, they are truly crystalline, and throughout the whole skeleton the crystallographic orientation is the same. After they have advanced a certain distance from their origin these primary branches throw out secondary branches as shown in Fig. 95, which proceed to grow at the same rate as the primary ones, so that at each point from which their growth begins the conditions at the origin are repeated. These secondary branches are

parallel to the corresponding primary ones and the crystallographic orientation of the atoms composing them is the same. The throwing out of secondary branches from the primary ones occurs at regular intervals as growth proceeds and at similar intervals tertiary branches are thrown out from the secondary. Although the primary branches are free to continue their growth, mutual interference occurs among the secondary and tertiary branches.

If the cross-sectional area and shape of the branches is neglected and attention confined to their axes, it is plain that when the growth of the skeleton has proceeded until it occupies a certain space the axes of the branches divide this space into cubes. The points at which branches are thrown out and those at which they meet are distributed in space like

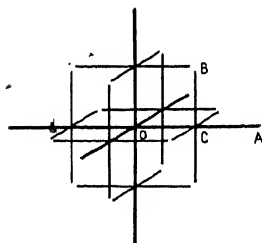


Fig. 95

the atoms in a simple cubic lattice. Furthermore, as all the branches may be supposed to grow at the same rate, their end points will be at equal distances from the origin when this distance is measured along the branches. Thus the length OA (Fig. 95) is equal to $OC + CB$, i.e. B and A are the same distance from O when the distance is measured in this way. A more extensive skeleton crystal is shown in

Fig. 96, all the end points of which are at equal distances from the origin. These form an octahedron as shown by the broken lines connecting the points A , B , C , D , E , and F in Fig. 96. Thus a skeleton crystal growing freely in a melt develops in such a way that at any stage in its growth it may be said to be contained within an imaginary octahedron.

The formation of a skeleton crystal like that shown in Fig. 96 is followed by a thickening of the branches, but there are great variations in the relations between these two processes. Two extreme cases are theoretically possible. On the one hand, an extensive skeleton consisting of primary, secondary, and tertiary branches may be formed before any thickening of the branches begins. On the other hand, the thickening may proceed concurrently with the growth of the skeleton and at such a rate that at all stages of growth the crystal resembles a compact solid rather than a skeleton. In practice the process of growth is intermediate between the two extreme cases, but it varies greatly from metal to metal and is affected by the rate of cooling and other factors. Thus in some cases it appears that thickening of the branches does not begin until growth of the skeleton is brought to a stop by contact with other crystals, while in other cases it seems to proceed almost concurrently with the growth of the skeleton.

If no factor other than the force of crystallization was in operation during the growth of skeleton crystals the branches would adopt a crystalline form, i.e. their cross-section would be regular and have flat sides and sharp corners. Surface tension, however, tends to reduce the surface

area of the branches to a minimum and in consequence sharp corners tend to be rounded off. There is no satisfactory method of measuring the surface tension of a solid but there is evidence that the surface tension of growing crystals is related to that of the liquid from which they grow. In any case the force of crystallization which tends to produce branches of regular cross-section is opposed by surface tension which tends to produce branches of circular cross-section and Desch (76) has pointed out that in the metals antimony and bismuth which have a

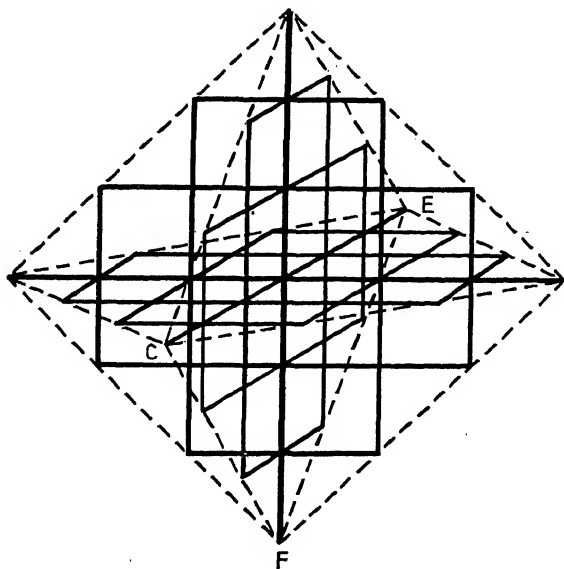


FIG. 96

low surface tension when molten, the branches of the skeletons have sharp angular outlines, while in copper and gold which have a high surface tension when molten the branches are rounded. Most of the metals resemble copper and gold, and in general the branches of skeletons are rounded.

While the individual branches in a skeleton crystal are surrounded by molten metal their shape is determined in the first instance by the relations between the force of crystallization and surface tension. It is also influenced, however, by the relative position of neighbouring branches for this determines the directions in which thickening may proceed. If an elaborate skeleton with closely spaced primary, secondary, and tertiary branches is formed, each branch will have regularly placed neighbours at short distances. Little thickening will be required before contact is established and at this stage the cross-section of the branches will be roughly circular. If, however, a simple skeleton is formed by the throwing out of a few widely spaced secondary branches, then each branch

will have plenty of room in which to thicken. In the course of this it will extend its cross-section in any direction in which it is free to grow and may in consequence become very irregular. Thus, disregarding the case in which a low surface tension permits branches of regular cross-section to grow, we may say that the form of the skeleton at the stage when the branches have thickened so as almost to fill space may vary between the following extremes: (1) the branches are close together and each must thicken within a limited space as a result of which they come into contact while their cross-section is approximately circular, (2) the branches are widely spaced and each has a considerable amount of room in which to thicken in the course of which process it may become very irregular in cross-section according to the supply of available liquid.

We have described the formation of the primary skeleton, the relations between the thickening of the branches and the growth of the skeleton, the cross-sectional shape of the branches in the early stages of thickening, and the irregular shapes that may be assumed at a later stage when the branches are originally widely separated. It remains to consider briefly the final stage in the growth of a crystal. This is controlled by the fact that the branches must finally thicken until the spaces that originally existed between them are filled. Until they come into contact the branches may have crystalline, circular, or irregular and rounded cross-sections, but such shapes do not completely fill space, and in the final stage of crystallization the branches will tend to become cellular in cross-section as a result of thickening until the requisite space is filled.

General Consideration of the Solidification of a Pure Metal.

In practice metals begin to solidify at the mould surface and the crystals tend to grow in the first instance along the temperature gradient between the outside and the inside of the cooling mass. Under these conditions the skeletons develop by advancing one primary branch in a direction perpendicular to the mould surface and throwing out secondary branches until they meet adjacent crystals growing in the same way. At a later stage, however, crystallization starts from nuclei distributed throughout the molten metal remaining in the interior of the mass. When this occurs the conditions under consideration in this chapter are realized. Each skeleton grows in three primary directions and throws out secondary and tertiary branches, and while it is growing freely the space over which it is spread has the shape of an octahedron. The growth of each skeleton is eventually arrested by its coming into contact with others, and thereafter its development is restricted to the formation of additional branches within its sphere of influence and to their thickening.

At the stage when contact is established between the different skeletons the spaces between the branches of each are filled with molten metal. Except in the case of bismuth the change from the liquid to the solid state is accompanied by a contraction, and consequently the amount of molten metal in the interstices of the skeleton is not sufficient to enable

it to thicken until the spaces between the branches are completely filled with solid. For this purpose a continuous supply of molten metal must percolate into the interstices of the skeletons. This takes place by the liquid moving downwards from the top, and it results in the formation of a cavity near the top of the solid metal. But as the interstices between the branches of the skeletons become smaller it becomes increasingly difficult for the requisite percolation to take place, and as a result liquid will not be supplied at every point where it is required. At such points, what are known as contraction cavities are formed when the available

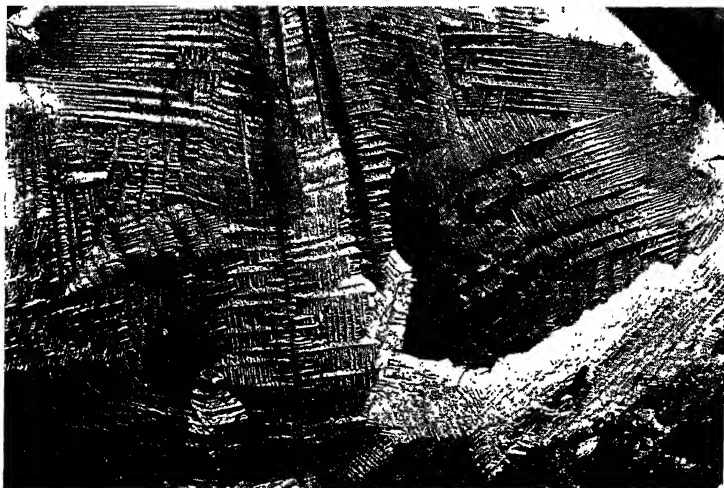


FIG. 97. Skeleton crystals on surface of cast antimony. $\frac{1}{4}$ natural size.

liquid solidifies, and these are responsible for the inferior mechanical properties of metal that has not been worked in comparison with metal that has. This is more fully discussed in Chapter IX. In so far as the available supply of molten metal allows, the filling in of the skeleton continues until all the interstices are closed, and as all the branches of each skeleton are parts of the same crystal, they coalesce and all evidence of their original individuality disappears. At the end of solidification the metal consists of a system of polyhedral grains each produced from a different nucleus. Their average size depends on the number of nuclei, and their shape is determined by their mode of growth, modified by interference between crystals growing from different centres.

When a section through a cast pure metal is polished, etched, and examined the structure observed is that of a system of polyhedral grains as shown in Fig. 4. There is nothing to show how the growth of those individual grains took place. Their mode of growth is frequently revealed, however, by the appearance of the top surface of a cast block; for owing to the contraction that accompanies solidification the primary skeleton is left in relief as shown in Fig. 97. Such crystals are described as dendritic.

The formation of skeleton crystals in pure metals appears to be due mainly to their great heat of crystallization. The heat evolved in the change from liquid to solid is generated at the surface of the growing crystals and by raising the temperature there it tends to delay crystallization. The heat is removed from the surface of the crystals by diffusion into the liquid and the rate at which it is dissipated determines the rate of growth. Heat is removed more rapidly from a solid angle than from an edge and more rapidly from an edge than a surface. In the first case it may be dissipated in all directions that radiate from the angle. In the second the number of directions in which it may be removed from a point on an edge is limited by the fact that heat is simultaneously being generated at all other points on the edge, while in the third case, as heat is being simultaneously generated from all points on the surface, that evolved at any given point can only be dissipated in a direction normal to the surface. It is therefore evident that the mode of growth most appropriate to the thermal conditions involves the development of skeleton crystals the branches of which provide many solid angles and edges, followed by the filling of the interstices when the extension of the skeleton is arrested. As already explained, the sharpness of the points and edges of the branches is in general reduced by the effect of surface tension.

CRYSTAL GROWTH IN RELATION TO THE STRUCTURE OF ALLOYS

In a pure metal the solid being formed remains the same from the beginning to the end of solidification. Every crystal consists of the same kind of atoms arranged in the same space-lattice and in each crystal every point is the same. This is not the case with alloys. If the two or more elements present form a solid solution each crystal in the solid contains all the elements in the same proportions as the alloy as a whole. But when the alloy has newly solidified the various elements are not uniformly distributed in each crystal. The process of solidification is such that the composition of the solid varies progressively from the beginning to the end. This process is described in detail later on. Meanwhile it is sufficient to state that owing to the way in which freezing takes place each layer deposited on the primary skeleton differs in composition from the preceding and succeeding layers. If all the elements present in the alloy do not form a solid solution, then two or more different constituents will be formed in the solid alloy. For the time being alloys containing two constituents will be considered. Solidification begins with the formation of primary skeleton crystals of one constituent, and when this has proceeded to the requisite extent the interstices are filled by the solidification of the other. In both types of alloys mentioned the way in which metal crystals grow is revealed when sections are polished and etched, but the actual structure observed depends on a number of factors, some of which will now be enumerated.

The growth of metal crystals takes place in three dimensions and microscopic examination of these is carried out on plane sections. In pure metals the grains finally formed are homogeneous crystals and a plane section through them gives a clear indication of their form. In alloys, however, the grains have complicated structures and a great variety of patterns may be obtained on plane sections through them. We may consider in the first place an alloy that solidifies as two constituents each of which is homogeneous. The relative proportions of the two constituents may vary within wide limits. Thus the growth of the primary skeletons of the first constituent may stop at any stage and solidification be completed by the formation of the other constituent. This may be regarded as a matrix in which the primary skeletons of the first constituent are embedded. The general three-dimensional structure of the alloy depends on the type of skeletons formed by the first constituent and on the extent to which their growth proceeds before the matrix begins to solidify. The structure observed on a plane section through any particular grain depends on the above factors and also on the relation of this to the three-dimensional skeleton.

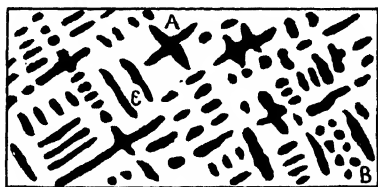


FIG. 98. Skeleton dark.

Let us first consider an alloy in which the development of the skeleton of the first constituent stops at a comparatively early stage. All the skeletons in the alloy may be considered to be similar, but when a section is cut and examined a considerable variety of patterns is obtained because each skeleton will be cut in a different direction relative to its branches and at a different point relative to its origin. If at any point the plane passes through the junction of branches of similar or different orders a cross like that shown at *A* (Fig. 98) will be observed. If the plane is nearly parallel to the plane containing the branches all the arms of the cross may be long. If, however, it is parallel to one branch and not to the other, two arms will be long and two short. If the plane examined cuts both branches obliquely, all the arms of the cross will be short. Where the plane examined cuts branches at points away from intersections, these appear as irregular rounded spots if cut nearly at right angles to their axes (*B*, Fig. 98), whereas they become more elongated as the angle between their axes and the plane decreases (*C*, Fig. 98). The various forms shown in this figure may be taken as representative of what is seen on a random section through a skeleton in an early stage of growth. The general structure bears little direct resemblance to the three-dimensional skeleton. Nevertheless, all the isolated forms in the figure are clearly related so as to form a pattern and this shows that they belong to one and the same skeleton. Micrographs of alloys showing structures of this kind are reproduced in Figs. 126 and 135.

If skeletons of the first constituent continue to form to a greater extent, the first consequence is an increase in the complexity of the patterns revealed in plane sections. Then as the branches thicken and the total volume occupied by the skeletons becomes equal to, or greater than, that occupied by the matrix, plane sections reveal the skeletons as connected wholes rather than as systems of apparently isolated parts. As already explained, however, the cross-sections of the branches tend to become more irregular as they thicken, and furthermore, this filling of the interstices of the skeletons may not take place simultaneously throughout the whole of one grain. It may begin near the origin and gradually spread outwards. As a result of the operation of these factors the structures revealed on plane sections through crystals in an advanced stage of

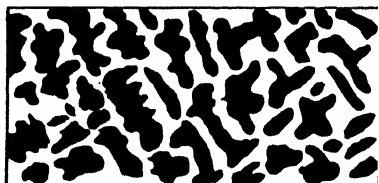


FIG. 99. Skeleton dark.

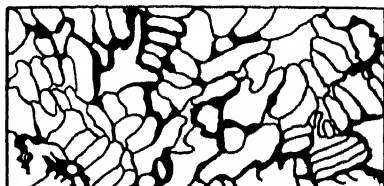


FIG. 100. Matrix dark.

growth tend to be less symmetrical than those on sections through less completely developed crystals. Thus structures like that shown in Fig. 99 are obtained. During growth, and while still surrounded by appreciable quantities of liquid, the branches of skeletons may take on rounded irregular shapes, but if their development is not brought to a stop by the solidification of a matrix constituent, they must continue to grow until they fill all the space between them. Rounded irregular shapes cannot fill space, and consequently, when the growth of the crystals reaches the stage at which the branches are extending into the minute spaces still separating them, the outline of the branches tends to become cellular. In a pure metal the branches eventually come into contact and coalesce, but if a small quantity of a second constituent solidifies between them when they have almost filled the intervening spaces, its distribution reveals the cellular form and the structures observed on plane sections are of the type shown in Figs. 100 and 548. Should the quantity of the second constituent be insufficient completely to outline the branches, it forms a discontinuous outline, and if it is present in still smaller amounts it is mainly located at crystal boundaries.

The structures seen on sections through cast alloys containing two constituents which solidify in turn are controlled by the factors described above. It now remains to describe those found in alloys that consist of one constituent which gradually changes its composition during the process of solidification. In an alloy of this type each three-dimensional crystal is formed by the development of a skeleton and the filling of the interstices with the same constituent. The composition of the crystal

varies progressively from the beginning to the end of its growth. The structures observed on plane sections through such crystals are influenced by the relations of the sections to the axes and origin of the crystals. In this case the etching reagent must be able to distinguish the variations in



g. 101. α -Brass: 66.6 per cent. Cu, 33.4 per cent. Zn.
As cast. $\times 100$.



FIG. 102. α -Bronze: 90 per cent. Cu,
10 per cent. Sn. As cast. $\times 50$.

composition in the individual crystals. The colour of each crystal is then seen to vary gradually from the skeleton first formed to the material deposited in the last remaining interstices. There are no sharp lines of demarcation between one part of the crystal and another, but simply a gradual change of colour that reveals its structure in a rather vague way. Certain alloys, such as those of gold-silver, copper-tin, and copper-zinc, show this more clearly than others, and the effect is brought out more clearly with objectives of high numerical aperture. Ordinary black

and white photomicrographs fail to reveal this gradation of colours, and with objectives of low numerical aperture it is not even seen by direct observation. Under these conditions the whole range of colours is divided



FIG. 103. Bronze: 75 per cent. Cu, 25 per cent. Sn.
As cast. $\times 100$.



FIG. 104. Cu-Ni alloy: 50 per cent. Cu, 50 per cent. Ni.
As cast. $\times 100$.

into two portions one of which appears light and the other dark. The crystal then appears as if it consisted of a primary skeleton of one constituent in a matrix of another and various sections through such crystals are shown in Figs. 101 to 104. If a solid solution alloy is maintained for a sufficient time at a temperature not far below that at which solidifica-

tion is completed, diffusion takes place in each crystal until its composition is uniform throughout. When this has taken place its structure cannot be distinguished under the microscope from that of a pure metal.

THERMAL ANALYSIS

While microscopic examination and X-ray analysis constitute the basic methods of studying solid alloys, thermal analysis is the basic method of studying the solidification and melting of metals and alloys. It is also an important method of studying constitutional changes in solid alloys. It depends on the fact that any change in state or constitution is accompanied by an energy change which is revealed by a heat evolution during cooling and a heat absorption during heating. It is carried out by taking time-temperature curves, usually during cooling.

When a body is cooling and no change is taking place, the curve connecting its temperature with time has a regular logarithmic form as illustrated by *A* (Fig. 105). If, however, the body concerned is a crucible containing molten metal the regular cooling will be arrested by the heat evolved when

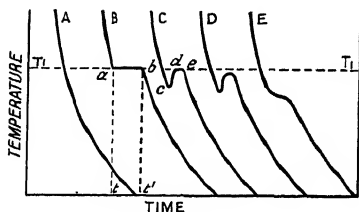


FIG. 105.

this metal solidifies. If no under-cooling of the molten metal occurs the curve will have the form illustrated by *B* (Fig. 105). The horizontal portion *ab* indicates that at the temperature T_1 the metal solidifies, and while this change is taking place the temperature is maintained constant by the heat evolved. After solidification is complete the metal again cools regularly and continues to do so if no transformations in the solid occur. As already explained, however, the beginning of solidification is always accompanied by a certain amount of under-cooling, i.e. the nuclei do not become sufficiently stable to serve as starting-points for crystallization until the melt is cooled to a temperature lower than the highest temperature at which solidification can proceed. Thus the actual cooling curve of a pure metal has the form illustrated by *C* (Fig. 105). The melt cools to *c* before crystallization proper begins, then the heat evolved raises the temperature to *d* and maintains this temperature for some time, after which cooling again proceeds.

The exact form of the curve after freezing has begun depends on the relations between the rate of abstraction of heat from the cooling metal and the rate of evolution of the heat of crystallization, which in turn depends on the rate of crystallization. If T_1 (Fig. 105) is the true freezing-point, i.e. the highest temperature at which solidification can proceed, then the evolution of heat accompanying crystallization cannot raise the temperature of the metal above this, for if it does crystallization,

and therefore heat evolution, is arrested. If solidification begins and continues at the temperature T_1 as represented by curve B (Fig. 105), the time interval $t-t'$ is the time required to abstract from the metal the heat evolved in solidification. In the case of a given mass of metal with a given heat of crystallization the time taken to abstract the heat evolved depends on the rate of its removal, and by increasing this the time interval $t-t'$ may be reduced.

The question arises, however, whether the rate of evolution of heat and therefore the rate of solidification always keeps pace with the rate of abstraction of heat. Solidification actually begins at some temperature below the true freezing-point, e.g. at c , curve C . If there is no limit to the rate of solidification other than that the temperature must not rise above T_1 , then, whatever the rate of abstraction of heat, the evolved heat will raise the temperature to T_1 and keep it there until solidification is complete. This is illustrated by the portion cde of curve C . If, however, there is some other limit to the rate of solidification, the conditions will be different. It appears that for each temperature below the true freezing-point there is a definite maximum rate of solidification. At the true freezing temperature this rate is comparatively slow. It increases as the temperature decreases, but below a certain temperature it begins to diminish again. Thus there is a maximum rate of solidification at each temperature and also a maximum rate for all temperatures. Increase in the rate of abstraction of heat may be secured by cooling a smaller mass of metal or by cooling in a medium that abstracts heat more rapidly than air. Such increases accelerate the rate of cooling of the melt and thus lower the temperature at which solidification begins. Furthermore, they result in a more rapid removal of the heat evolved during solidification. Since the rate at which solidification can take place at the true freezing temperature is limited, and since it can proceed more rapidly at temperatures below this, it follows that when heat is being extracted rapidly the temperature of the melt will not rise to the true freezing-point. Thus a cooling curve of the type represented by D (Fig. 105) is obtained. A further increase in the rate of abstraction of heat may give rise to a cooling curve such as E (Fig. 105), which shows that the relations between the abstraction and evolution of heat are such that the temperature continues to fall while solidification is in progress. Cooling curves like this have not been obtained for solidifying metals, but something of this nature probably occurs when small drops of molten metal are immersed in water. Even under these conditions, however, freezing is complete before the temperature falls to the point at which the rate of solidification is a maximum. It is, in fact, impossible to cool a metal below this temperature while it is still wholly or partly molten. If this could be done it could then be retained at atmospheric temperature in a molten condition. Transformations occurring in solid alloys can be suppressed in this way but not solidification.

It follows from the above that the rate of solidification increases with

the rate of abstraction of heat, and solidification proceeds to completion no matter how rapid the cooling. At the same time, however, the temperature at which solidification begins and continues is lowered by increasing the rate of cooling. Lowering the range in which freezing takes place increases the number of nuclei formed, and it is this that explains some of the increase in the rate of solidification. It also accounts for the fact that the average size of the crystals in the solid metal decreases as the rate of cooling increases.

Cooling curves of the type described above and illustrated in Fig. 105 are known as direct curves and in constructing them time is plotted against temperature. Such curves are suitable for studying the solidification of pure metals, for in these cases substantial amounts of heat are evolved within narrow ranges of temperature. Their chief disadvantage is that when no change is taking place in the metal under examination the curve tends to become progressively less steep as the temperature falls. To plot a complete curve from above the melting-point to the ordinary temperature requires a very close time scale. This tends to diminish the effect of heat evolution at high temperatures, and at low temperatures, when the natural curve is becoming almost parallel to the time axis, changes in form resulting from the liberation of heat by the metal cannot be detected. During the solidification of alloys the liberation of heat is frequently spread over a considerable range of temperature, and transformations in the solid are accompanied by heat evolutions that are small compared with those accompanying solidification. In order to study such changes it is necessary to plot cooling curves in such a way that the natural decrease in cooling rate with falling temperature is reduced, while a retardation of cooling due to a transformation in the metal is magnified.

One method of attaining this object is to plot what are known as 'inverse-rate' curves in which temperature is taken as the ordinate (as in Fig. 105), and the time taken for the temperature to fall through successive equal intervals is taken as the abscissa. Thus in plotting such a curve a suitable temperature interval of 2° or 5° is selected and the times taken for the temperature to fall through successive intervals are plotted against temperature. Another method is the 'difference method' in which the metal under study cools alongside another sample that undergoes no change in the temperature range under investigation. The temperature of the metal under test is plotted against the difference in temperature between it and the inert sample. If no change takes place there is no difference between the temperatures of the two specimens at any moment and the curve plotted is a vertical line. But if an evolution of heat in the metal occurs it delays its cooling and the resulting difference in temperature appears on the curve as a departure from the vertical. Evolutions of heat are further magnified by using the 'derived differential' method of plotting the 'difference curve'. In this case temperature is plotted against the slope at each point of the curve

showing the difference in temperature of the two samples. Thus if T is the temperature of the metal under investigation and T_1 that of the inert sample, the difference curve is obtained by plotting T against $T - T_1$ while the derived differential curve is obtained by plotting T against $\frac{\Delta(T - T_1)}{\Delta T}$.

Fig. 106 prepared by Desch (7) shows the cooling curve of a certain alloy plotted in the four ways described above.

ALLOY SYSTEMS

The alloys that may be made by mixing a number of metals in progressively varying proportions constitute a system. If two metals only are involved, all the alloys that can be made by mixing them in various proportions between 100 per cent. of one metal and 100 per cent. of the other constitute a binary system. If three or four metals are involved the resulting alloy systems are known as ternary and quaternary systems respectively. In considering the solidification of alloys it is advisable to consider systems rather

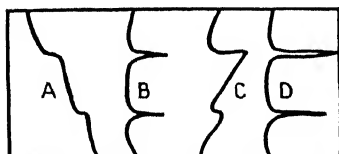


FIG. 106. Cooling curves. A, Direct.
B, Inverse-rate. C, Difference.
D, Derived differential.

than individual alloys, and attention will now be given to the solidification of binary alloys formed by metals that are completely miscible when molten. For convenience of reference the various types of binary system are given a number.

Type 1. The Two Metals are Completely Miscible when Liquid and Completely Immiscible when Solid.

In alloy systems of this type the two metals may be mixed in any proportions to form a homogeneous liquid, but when they solidify the component metals separate and each forms its own particular crystals. An example is provided by the alloys of zinc and tin. Pure zinc freezes at 419.4°C . and pure tin at 231.9°C . If an alloy containing 92.1 per cent. of tin and 7.9 per cent. of zinc is made it freezes at 198°C . and crystals of the two metals grow simultaneously from the melt. This particular alloy is known as the eutectic alloy, and owing to the fact that crystals of both metals grow at the same time, neither is able to crystallize in its natural way with the development of skeletons followed by the filling of the interstices. Instead, the simultaneous growth of the two kinds of crystals leads to the production of a particular arrangement known generally as a eutectic structure. Structures of this type are described later.

All other alloys in this system solidify over a range of temperature. If, e.g., an alloy containing more than 7.9 per cent. of zinc is made up, it begins to freeze at a temperature higher than 198°C . (the eutectic

temperature) and lower than 419.4°C . (the melting-point of zinc). If it contains, say, 60 per cent. of zinc it begins to freeze at 360°C . and the crystals that start to grow consist of pure zinc. As a result the proportion of zinc in the liquid is decreased while that of tin is increased. This change in the composition of the melt lowers the temperature at which solid can form. When the temperature falls, however, more zinc solidifies, and in general the freezing of zinc continues as the temperature falls with consequent decrease in the zinc content of the melt. The conditions are such that when the temperature has fallen to 198°C . the proportion of zinc has been reduced to 7.9 per cent., and the residual liquid then solidifies at

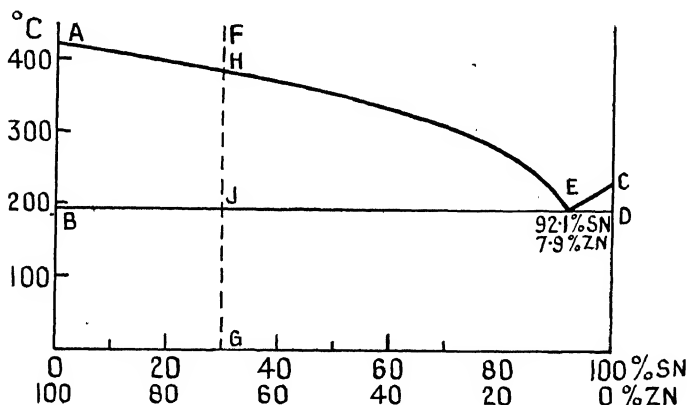


FIG. 107.

constant temperature with the production of a eutectic structure of zinc and tin crystals. All alloys containing more than 7.9 per cent. of zinc solidify in the above manner. The temperature at which freezing begins rises from 198° to 419.4°C . as the zinc content is raised from 7.9 to 100 per cent. At the same time the proportion of the alloy that solidifies as pure zinc increases from 0 to 100 per cent., while the proportion that solidifies as the eutectic decreases from 100 to 0 per cent. Similar conditions obtain in alloys that lie on the other side of the eutectic, i.e. contain more than 92.1 per cent. of tin. In this case the temperature at which freezing begins rises from 198° to 231.9°C . as the tin content is increased from 92.1 to 100 per cent. At the same time the proportion of the alloy that solidifies as pure tin increases from 0 to 100 per cent. whereas the proportion that solidifies as eutectic decreases from 100 to 0 per cent.

If cooling curves are taken of a series of zinc-tin alloys and the temperatures at which freezing begins and ends are plotted against composition, the diagram shown in Fig. 107 is obtained. This diagram shows: (1) that the eutectic alloy *E* freezes at 198°C .; (2) that alloys on the zinc side of the eutectic (the left) begin to solidify at the appropriate point on the line *AE* and are completely solidified at 198°C . (line *BD*);

and (3) that alloys on the tin side of the eutectic begin to solidify at the appropriate point on the line CE and are completely solidified also at 198°C . This figure is known as the constitutional diagram of the tin-zinc system and some important inferences can be drawn from it.

The composition of any alloy in the system is represented by a point on the horizontal axis, and as it does not change with temperature it may also be represented by a vertical line such as FG . By following this line it is possible to discover from the diagram the constitutional changes which this alloy undergoes. Above H it is molten, but at this point it begins to solidify and crystals of pure zinc grow. Some liquid remains,

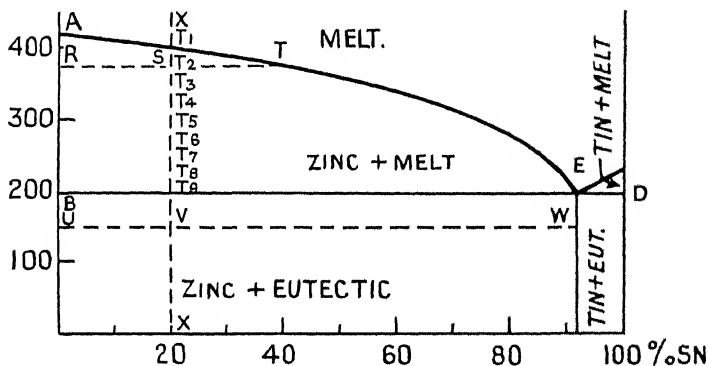


FIG. 108.

however, until the alloy cools to J when solidification is completed by the formation of eutectic. Below this point no changes occur. On heating from atmospheric temperature the reverse changes take place, i.e. the eutectic melts at J , as the alloy is heated from J to H primary zinc crystals dissolve in the melt, and at H melting is complete. A line such as FG may be drawn to represent any alloy and its changes may be followed as above. In general, if the composition and temperature of an alloy are represented by a point, it is (1) completely molten if the point lies above AEC , (2) completely solid if it lies below BD , and (3) partly molten and partly solid if it lies in the areas AEB or CED . In order to furnish all the information that can be obtained from the diagram by regarding it in this way it is sometimes convenient to mark in each area the phases stable there as shown in Fig. 108.

From a knowledge of the way in which metal crystals grow from a melt and of the fact that the simultaneous formation of two kinds of crystals at the eutectic point results in a particular arrangement of them, it is possible also to infer from the diagram something about the structure of the alloys. Thus, if an alloy contains a very high proportion of zinc, crystals of this metal will grow in their characteristic manner until solidification is almost completed, when the small quantity of residual liquid will solidify as eutectic and outline the structure of the primary

crystals as shown in Fig. 100. If the zinc content is less, the solidification of the eutectic will take place before the growth of the zinc crystals has reached the above stage and the resulting structure will resemble that shown in Fig. 99. If the zinc content is not much above that of the eutectic alloy, then the growth of the zinc crystals will be arrested at an early stage by the formation of eutectic and the structure obtained will resemble that shown in Fig. 98. Finally, if the zinc content is exactly 7.9 per cent., no primary zinc skeletons will form at all and only the eutectic will be present in the solid alloy. The structures formed by alloys containing tin in excess of the eutectic proportions may be described in a similar way.

The lines AE and CE (Fig. 107) are obtained by determining the beginning of solidification in alloys of different composition by means of cooling curves. The temperatures plotted are not the lowest temperatures to which the melts cool before solidification begins. These are affected by under-cooling, and for the purpose of a diagram such as Fig. 107 the temperatures plotted are those to which the melts rise after solidification has begun. As

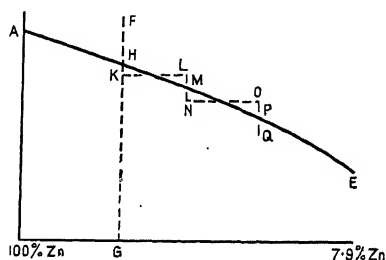


FIG. 109.

slow rates of cooling are used in determining these diagrams, the latter temperatures are the highest at which solidification can proceed in the alloys concerned. Neglecting under-cooling, we can say that in an alloy containing 70 per cent. of zinc and 30 per cent. of tin solidification begins at H (Fig. 107). By the time the temperature has fallen to K (Fig. 109) a certain amount of pure zinc has solidified, and as a result the composition of the liquid portion of the alloy is moved towards the right, e.g. to L (Fig. 109). The composition of the alloy as a whole (solid plus liquid) remains the same, but at the temperature of K this is made up of a mixture in the requisite proportions of pure zinc (solid) and liquid of the composition L . M is the highest temperature at which solid can form from liquid of this composition, and therefore the alloy must cool before more solid can form. A further small amount of zinc solidifies as the alloy cools from M to N and the composition of the liquid is moved towards the right, say, to O . Then more solid is formed from liquid of the composition O as the alloy cools from P to Q , and so on.

The process described above is called 'Selective Freezing' and is of great importance in the study of alloys. It has been described as if it occurred in steps of considerable magnitude. Actually, however, it is a continuous process. As there is no under-cooling except at the very beginning of solidification this need not be taken into account. It follows, therefore, that some solid is formed immediately the melt cools to H ,

and as the amount formed is very small the composition of the melt is moved only a small distance towards the right. A slight fall in temperature results in the formation of a further small amount of solid and so the process continues. In order to illustrate what actually occurs the large steps shown in Fig. 109 may be regarded as becoming smaller and smaller until they are indistinguishable from the continuous line HP . Thus it can be said that in the alloy under consideration solidification begins at H and continues as the temperature falls. Meanwhile crystals of pure zinc grow and the liquid changes in composition along the line HE . In any other alloy on the zinc side of the eutectic the same process occurs, the only difference being that solidification begins at a different point on AE . A similar process occurs in alloys on the tin side of the eutectic, except that tin crystals are formed and the liquid changes in composition along the line CE (Fig. 107).

The true significance of the line AE is that any point on it indicates the composition and temperature of the liquid that can exist in equilibrium with solid zinc crystals. Thus at the temperature of the point M liquid of the composition M can exist in equilibrium with solid zinc, i.e. no change will take place with time if the other conditions are not altered. If, however, we heat the liquid, zinc will dissolve and the composition of the liquid will move along MA . If we cool the liquid, zinc will be deposited and the composition will move along ME . So long as solid zinc is in contact with a molten solution of zinc and tin the composition of this solution will lie on the line AE . The line CE has a similar significance with regard to the relations between solid tin and a solution of zinc and tin. The significance of point E derives from the fact that it lies on both lines (AE and CE) and is therefore the point at which a liquid solution of zinc and tin is in equilibrium with solid zinc and solid tin. No matter what liquid we start with, if we cool it, either zinc or tin will separate from solution so that when the temperature reaches 198°C . the liquid contains 92.1 per cent. of tin and 7.9 per cent. of zinc. If we try to cool it further, zinc and tin will crystallize simultaneously and the heat evolved will prevent the temperature falling below 198°C . until all the liquid has disappeared. Line BD (Fig. 107) is a horizontal drawn through E in order to show that in all alloys solidification is completed and melting begins at this temperature. This divides the range in which the alloys are completely solid from that in which they are partly liquid and partly solid (see Fig. 108) and it is known as the 'solidus': AEC divides the range in which the alloys are completely liquid from that in which they are partly liquid and partly solid and is known as the 'liquidus'. ✓

Attention may now be turned to the quantitative implications of the diagram under consideration. At temperatures above T_1 (Fig. 108) the alloy X is completely molten. At T_1 it begins to solidify and at T_2 it consists of a mixture of solid zinc (composition R) and liquid (composition T). These two phases are present in such proportions that the whole

alloy contains 20 per cent. of tin and 80 per cent. of zinc, and it can be shown that the ratio of the amount of liquid to that of solid is given by the ratio of RS to ST . Thus

$$\frac{\text{amount of liquid}}{\text{amount of solid}} \cdot \cdot \frac{RS}{ST}$$

$$\frac{\text{amount of liquid}}{\text{amount of alloy}} \cdot \cdot \frac{RS}{RT}$$

$$\frac{\text{amount of solid}}{\text{amount of alloy}} \cdot \cdot \frac{ST}{RT}$$

As the temperature falls from T_1 to T_9 the proportion of liquid decreases from 100 to about 21.74 per cent. while the proportion of solid increases from 0 to 78.26 per cent. The remaining liquid solidifies at T_9 (198° C.) by the formation of eutectic. At all temperatures below 198° C. the alloy consists of 78.26 per cent. by weight of primary zinc crystals and 21.74 per cent. of eutectic. The relative proportion of zinc and eutectic is given by the ratio of the segments WV and VU of the line WU . It is evident that as we move the line XX towards the left the proportion of primary zinc crystals increases (WV increases), and as we move it towards the right the proportion of eutectic increases (VU increases). In general, as the composition of the alloy varies from 100 to 7.9 per cent. of zinc the proportion of primary zinc crystals falls from 100 to 0 per cent. and the proportion of eutectic rises from 0 to 100 per cent. The constitution is a linear function of the composition. The same applies to the tin side of the eutectic.

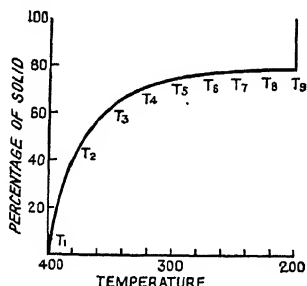


FIG. 110.

The amount of solid formed in successive equal temperature intervals in the range of solidification can also be deduced from the constitutional diagram. If in the case of alloy X , Fig. 108, a number of temperatures separated by small intervals such as T_1, T_2, T_3, T_4, T_5 , &c., are taken and horizontal lines such as RST are drawn at each temperature, the total amount of solid existing at each may be determined by the method described above. At T_2 , e.g., the total amount of solid metal is to the total weight of alloy as ST is to RT . If this is done for the temperatures shown, a curve may be plotted indicating the respective amounts of solid and liquid existing at each temperature. Such a curve for alloy X containing 20 per cent. of tin is shown in Fig. 110. From this the amount of solid formed in successive equal temperature intervals may be deduced. It is evident that when solidification begins, the amount of solid formed in a given interval of temperature is a maximum, and that thereafter it

decreases progressively until the eutectic temperature is reached, when the remaining liquid—in this case 21.74 per cent. of the whole—solidifies. The reason for the decrease in the amount of solid zinc formed in successive temperature intervals is that the quantity of residual liquid is constantly diminishing, and the formation of a progressively decreasing quantity of solid is required to produce a given change in its composition.

The above consideration has an important bearing on the shape of cooling curves. Those shown in Fig. 106 relate to an alloy of the type under consideration, yet they show two changes, whereas actually solidification proceeds progressively from the beginning to the end. Two peaks are obtained on cooling curves because large amounts of solid are produced within narrow temperature ranges at the beginning of solidification and at the eutectic point. In the intervening temperature range smaller quantities of solid are formed and smaller amounts of heat are evolved. Thus, cooling curves give the impression that no solid is forming in the intervening range. Failure to appreciate the reason for the first peak on cooling curves like those shown in Fig. 106 has sometimes resulted in a misunderstanding of constitutional diagrams.

One further point remains to be dealt with. The line *BD* in Figs. 107–8 is drawn right across the diagram and therefore suggests that when an infinitely small amount of either metal is added to the other solidification takes place over a considerable range instead of at a particular temperature. Pure zinc, for example, solidifies at 419.4°C ., and according to Fig. 107 the addition of even the smallest amount of tin should cause solidification to extend from 419° to 198°C . Such a sudden change in behaviour may well be doubted, and it is necessary to point out that *BD* should not be extended to the extreme sides of the diagram. This figure is constructed on the assumption that in the solid state each of the metals is completely insoluble in the other. But this condition is probably never realized, and owing to some degree of solid solubility the line *BD* does not extend to the sides of the diagram. In certain systems, however, the solid solubility of the metals in each other is so small that it cannot be determined and is usually neglected in considering alloys made from them.

PRIMARY SOLID SOLUTIONS

In the types of alloy systems now to be considered the solid solubility of the metals cannot be neglected and it is therefore necessary to consider what this is. Before doing so, however, it may be explained that the degree of mutual solid solubility exhibited by different pairs of metals varies considerably. Beginning with alloys such as those of zinc and tin in which it is extremely small we can find alloys exhibiting all degrees of it up to complete miscibility in the solid state. The factors that determine the extent to which one solid metal dissolves another are considered later, but whatever the extent of the solubility the crystal

structure of the resulting solution corresponds with one of the types described below.

When one solid metal dissolves another a solid solution is formed, and this type of alloy constituent is sometimes called a primary solid solution to distinguish it from another type described in a later section and sometimes called a secondary solid solution. In the former the crystal structure is that of the predominant (solvent) metal and the atoms of the other (solute) element are incorporated in it. If the incorporation of the solute atoms takes place in such a way that they are substituted for solvent atoms in the crystal structure the solution is described as 'substitutional'. If, however, they take up positions in the interstices of the space-lattice formed by the atoms of the solvent metal the solution is described as 'interstitial'.

Most primary solid solutions are of the substitutional type and a good example is the solution of zinc in copper. Pure copper has a face-centred cubic lattice and pure zinc a close packed hexagonal lattice. If the two metals are mixed in any proportions between 0 and 38 per cent. of zinc, the solid alloy consists at atmospheric temperature of crystals of one kind only. Each crystal contains both zinc and copper atoms in the proportions in which they were mixed. The space-lattice of the crystals is face-centred cubic like that of copper, but as the zinc content is increased from 0 to 38 per cent. an increasing number of the lattice points are occupied by zinc instead of copper atoms.

Some primary solid solutions are of the interstitial type and the best-known is the solution of carbon in γ -iron. At $1,100^{\circ}\text{C}$. γ -iron can dissolve up to 1.7 per cent. of carbon, and alloys within this range of composition consist of crystals of one kind only. Each crystal contains iron and carbon in the proportions in which they are present in the alloy. The space-lattice of the crystals is face-centred cubic like γ -iron and the carbon atoms are not substituted for iron atoms at lattice points but are situated in the interstices of the lattice. Solid solutions of this type are rare compared with those of the substitutional type. They are known to be formed, however, when one of the transition elements, viz. Ti, V, Cr, Mn, Fe, Co, Ni, &c., dissolves an element the atoms of which are small, e.g. H, C, or N. In alloys containing three elements it is possible to have a combined substitutional and interstitial solid solution. When, e.g., manganese and carbon are alloyed with iron, the manganese atoms are substituted for iron atoms at lattice points while the carbon atoms are situated in the interstices.

One of the principal characteristics of a primary solid solution is that its space-lattice is of the same type as that of the basis metal. The dimensions of the unit cell vary, however, with the composition. Thus, while the length of the side of the unit cell in pure copper is 3.6078 \AA ., in an alloy containing 38 per cent. of zinc it is 3.693 \AA ., and while the lattice constant of pure silver is 4.078 \AA ., that of silver with 8 per cent. of copper in solid solution is 4.029 \AA . The replacement of one kind of

atom by another may thus increase or decrease the size of the unit cell. Now the density of a pure metal or primary solid solution may be calculated from the volume of the unit cell, the number of atoms per cell, and the atomic weights of these atoms, and as the last two factors are constant the specific volume is directly proportional to the lattice constant. When the specific volumes of primary solid solutions were first studied it was concluded that they were linear functions of the composition, i.e. that the volume of a given solution could be calculated from those of the pure metals composing it. This was called the 'additivity' or 'mixture' law, and in terms of lattice constants it means that if two elements form a primary solid solution the lattice constant should vary linearly with the atomic composition. Specific volumes calculated from lattice constants approach more nearly the true values than those determined in other ways, and recent determinations of these constants show that while the additivity law is frequently obeyed, deviations are not uncommon. The subject is reviewed by Jette (77) and the following illustrations are taken from his paper.

Many pairs of metals are completely miscible in the solid state, i.e. all their alloys are primary solid solutions and there is no sharp distinction between the solution of *A* in *B* and that of *B* in *A*. For such conditions to be realized it is obvious that the two metals must have the same crystal structure otherwise a gradual transition from the space-lattice of one to that of the other would not be possible. Many solid solutions of this type obey the additivity law, e.g. Au-Pt, Au-Pd, Mo-W, Pt-Ir, Pt-Rh, &c. Negative deviations from the law have been found, however, in Au-Ag, Ag-Pt, Ag-Pd, and Cu-Ni, positive deviations in Cu-Au and Cu-Pd, and both positive and negative deviations in Fe-Cr. In the case of the Au-Ag solid solutions the deviation is striking. The lattice constant of pure gold is 4.070 Å. and of pure silver 4.078 Å. If the alloys obeyed the mixture law the lattice constant of a solution containing 60 atomic per cent. of gold and 40 atomic per cent. of silver would be 4.073 Å. Actually it is 4.067 Å., and the curve connecting lattice constant and atomic composition slopes downwards from both ends to this value. In the iron-chromium solid solutions the lattice constants lie above the additivity line at the iron end and below it at the chromium end of the system. Many pairs of metals that have the same crystal structure are only partly miscible in the solid state, i.e. *A* is soluble in *B* up to a certain limit and *B* is soluble in *A* up to a certain limit. The Cu-Ag alloys are an example. At the temperature of solidification silver can dissolve 8.8 per cent. of copper and copper can dissolve 8.0 per cent. of silver. In both these ranges of solid solubility positive deviations from the additivity law are observed.

When we come to consider solid solutions formed by pairs of metals that have different crystal structures, account must be taken of the 'co-ordination number'. An atom of a metal that crystallizes in the body-centred cubic system has eight equidistant neighbours. The

co-ordination number for this lattice is 8. In the face-centred cubic and close packed hexagonal lattices each atom has 12 equidistant neighbours and the co-ordination number is 12. It has been shown by Goldschmidt that the effective radius of an atom increases with the co-ordination number of the lattice of which it forms part. Thus, if a body-centred cubic metal dissolves in a face-centred cubic metal, the effective radius of the atoms of the body-centred metal will be greater in the solid solution than in the body-centred crystals. Assuming that when an atom normally possessing a certain co-ordination number enters a lattice in which its co-ordination number is different, the change in its effective radius is such that the volume per atom remains the same, it is possible to calculate the correction that must be used to make the additivity law apply to such cases. The calculated correction factors are considered by Jette, who also compares the corrected mixture law atomic radii of certain solid solutions with the experimentally determined values. He shows that deviations from the mixture law are obtained in Au-Fe, Ni-Cr, and Cu-Mn solid solutions.

The Solidification of a Primary Solid Solution.

The change from a liquid to a solid solution might be expected to be a simple transformation. Actually it is quite complicated and involves three processes, viz. (1) Selective Freezing, (2) Solid Diffusion, and (3) Diffusion from Liquid to Solid. The first of these proceeds in much the same way whatever the rate of cooling. The extent to which the second proceeds depends on the rate of cooling, and the progress of the third depends on that of the second.

All copper-nickel alloys solidify as primary solid solutions and the change from the liquid to the solid state may be illustrated in the case of an alloy containing 50 per cent. of each metal. This alloy begins to solidify at $1,320^{\circ}\text{C}$. The solid first formed is neither pure nickel, nor pure copper, nor a solid solution of the same composition as the melt. In general the composition of the solid solution that first solidifies is such that the resulting change in the composition of the melt lowers its freezing-point. In the case under consideration the first formed solid contains more nickel and less copper than the melt. This is illustrated in Fig. 111 in which *XX* represents the composition of the alloy, *A* the point at which solidification begins, and *B* the composition of the first formed solid. Owing to the formation of a small quantity of solid of this composition the copper content of the melt is increased and its composition is therefore moved towards the right, i.e. to *C*. As liquid of composition *C* has a lower freezing-point than liquid of composition *A* no more solid is formed until the temperature falls to *D*. At this point more solid is formed, and as the copper content of the melt is greater than at *A*, the solid formed contains more copper than that first formed, i.e. it is of composition *E*. Owing to the formation of this solid the composition of the melt is moved to *F*, and when the temperature falls

to G solid of composition H is formed. In this way selective freezing proceeds.

As explained in connexion with Fig. 109 the pronounced steps shown in Fig. 111 are assumed for the purpose of description. Selective freezing is, however, actually a continuous process, i.e. it is made up of steps so small that they are indistinguishable from a smooth line. Thus it can be said that in the alloy XX solidification begins when the liquid is cooled to A and continues as the temperature falls. Meanwhile the composition of the melt moves along the line $ADGJ$ and solid of progressively varying composition is produced along $BEHK$. The significance

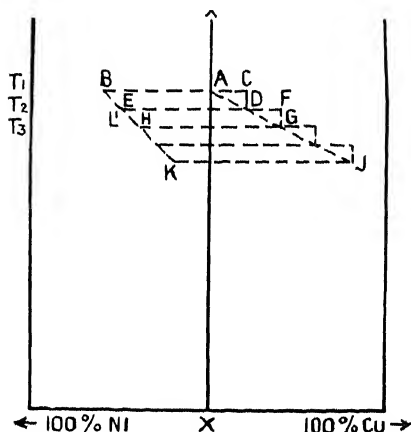


FIG. 111.

of these lines is that any point on $ADGJ$ indicates the composition and temperature of the liquid that can exist in equilibrium with the solid represented by a horizontally opposite point on $BEHK$. Thus at the temperature T_1 liquid of composition A can exist in equilibrium with solid of composition B , and at the temperature T_2 liquid of composition D can exist in equilibrium with solid of composition E .

In order to consider solid diffusion and the various other processes involved, and to explain their relation to selective freezing, it is necessary to revert to the

idea of steps. Suppose, e.g. that the alloy cools quickly from T_1 to T_2 and that the temperature is then maintained constant. During cooling the composition of the liquid will move from A to D and crystals of progressively varying composition will be produced. At T_2 the composition of each crystal will vary from B to E and the average composition of each will be L . While the temperature is maintained constant diffusion within the solid takes place, i.e. nickel diffuses from the regions where its concentration is high to those where it is low and copper diffuses in a similar manner. If sufficient time is allowed, this solid diffusion will establish a uniform distribution of the two metals in each crystal. Furthermore, if no other change takes place, the uniform composition thus reached will be L , the average composition of the solid when it first reached T_2 . But liquid of composition D cannot exist in equilibrium with solid of composition L at the temperature T_2 . It can only exist in equilibrium with solid of composition E , and consequently, while diffusion within the solid is producing a uniform composition, copper is diffusing from the liquid to the solid to maintain the composition of the outer layer of the crystals at E . When, therefore, the crystals do attain a uniform composition, this is E and not L , the extra copper

required being obtained by diffusion from the liquid. Obviously this diffusion of copper from the liquid will tend to move its composition to the left. But at T_2 the only liquid that can exist in equilibrium with solid has the composition D . Thus, as copper diffuses from the liquid to the solid, and tends to move the composition of the liquid to the left, more solid of composition E is formed and tends to move the composition to the right. These two changes are so adjusted that the composition of the liquid remains at D so long as the temperature remains at T_2 .

It follows from the above that if the temperature falls quickly from T_1 to T_2 and is then maintained constant at T_2 , the following changes take place at constant temperature: (1) diffusion in the solid, (2) diffusion from liquid to solid, and (3) the formation of more solid. During these changes the liquid remains of uniform composition D , while the solid changes from a composition varying from B to E to one corresponding to E itself. When this condition is reached no further change takes place, while the temperature is maintained constant. The whole alloy is in a state of equilibrium at T_2 . If cooling is supposed to take place in steps, such that the temperature falls quickly through small intervals and then remains constant until equilibrium is established, each step will be similar to the one just described, and when equilibrium is reached the composition of the liquid as a whole will be represented by a point on $ADGJ$ and that of the solid as a whole by a point on $BEHK$. If, however, the time for which the temperature is maintained constant after each small drop is less than that required to reach equilibrium, then the composition of the liquid as a whole will still be represented by a point on $ADGJ$, and that of the solid in immediate contact with the liquid by a corresponding point on $BEHK$, but the composition of the rest of the solid will lie to the left of $BEHK$.

If the steps described above are supposed to be very small they become the same as continuous cooling, and the effects of different rates of cooling may now be considered. Selective freezing is not appreciably affected by time, i.e. by the rate of cooling. No matter how rapidly the temperature falls the formation of solid proceeds, the composition of the melt moves along $ADGJ$ and solid of progressively varying composition is deposited along $BEHK$. Solid diffusion is, however, a relatively slow process and the extent to which it takes place depends on time. The other changes, viz. diffusion from liquid to solid and the formation of more solid to balance the change in composition resulting from this diffusion, depend on solid diffusion and are therefore affected by time.

We may begin by considering very slow cooling such that equilibrium is established at each step. The lines AJ and BK , Fig. 112, have the same significance as $ADGJ$ and $BEHK$ in Fig. 111. In the alloy XX solidification begins at A and proceeds as the temperature falls. The liquid changes in composition along AJ and solid of varying composition is formed along BK . Under the assumed conditions diffusion within the solid keeps pace with the formation of solid so that at any instant the

composition of the solid is uniform. Thus points on line BK , besides representing the composition of the solid being formed, also represent the composition of all the solid existing at any given temperature. Before solidification begins the composition of the liquid is the same as that of the alloy. While it proceeds the solid contains more than 50 per cent. of nickel and the liquid more than 50 per cent. of copper, but the relative proportions of these two phases are such that the alloy as a whole contains 50 per cent. of each metal. When solidification is complete the composition of the solid is the same as that of the alloy, and as BK represents the composition of the solid existing at any temperature,

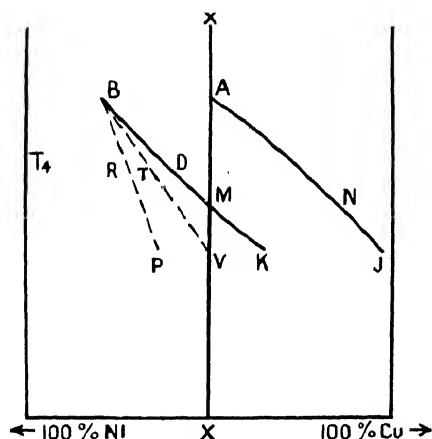


FIG. 112.

solidification is complete when it cuts XX , i.e. at M , and the composition of the last liquid to solidify is N .

The final stage of solidification requires more detailed consideration. According to Fig. 112 it involves the formation of solid of composition M from liquid of composition N . Obviously such a change could not result in the disappearance of the last drop of liquid, and actually the most important feature of this stage is diffusion of copper from the liquid to the solid. Throughout the whole process of solidification the

deposition of solid of a composition represented by the appropriate point on BK is accompanied by diffusion of copper from liquid to solid. During each small drop in temperature from T_x to T_y this brings the copper content of the solid that existed in equilibrium with liquid at T_x up to that required for equilibrium at T_y . As solidification proceeds the amount of solid increases and greater amounts of copper must diffuse in order to effect this change. At the same time the amount of liquid decreases and the diffusion of a given amount of copper in this way has a greater effect on its composition. Towards the end of freezing the amount of liquid transformed to solid by the diffusion of copper into the solid becomes greater than that transformed by deposition. The last stage in solidification, therefore, involves the diffusion of a considerable amount of copper into the solid and the deposition of a small quantity of solid of the composition M . In this way the last small drop of liquid disappears. ✓

In practice the rate of cooling through the range of solidification is rarely slow enough to permit equilibrium to be maintained. Consequently diffusion in the solid does not keep pace with the formation of solid. In the alloy XX , Fig. 112, the solid first formed is of composition

B and that subsequently formed varies in composition along BK . Under practical conditions the amount of copper that diffuses into the solid is not sufficient to raise its copper content along BK . But some diffusion does take place and the first formed solid may be supposed to change in composition along BP . Each small quantity of solid formed changes in a similar way. At the temperature T_4 , e.g., the composition of the solid varies between R and D while the average is T . At every other temperature in the range of solidification the composition of the solid varies between that represented by the appropriate point on BK and the corresponding point on BP . The average composition is represented by the appropriate point on BV . Solidification is complete when the average composition of the solid is the same as that of the alloy, i.e. when BV cuts XX . At this point the liquid is of composition J and the solid varies in composition between K and P .

The case considered above may be regarded as the general one. BP represents the change in composition of the solid that contains least copper, i.e. the first formed solid. BK represents the composition of the solid successively formed as the temperature falls, and BV represents the average composition of the solid. BK is unaffected by the rate of cooling, but the slope of BP depends on the amount of copper diffusing into the first formed solid and this in turn depends on time. As the rate of cooling is decreased, BP (and therefore BV) approaches nearer to BK , and when the rate is slow enough to permit equilibrium to be maintained all the lines coincide. As the rate of cooling is increased, BP (and therefore BV) swings farther away from BK and as a result BV cuts XX at a lower temperature, the variation in composition within each crystal increases, and the composition of the last drop of liquid to solidify moves farther along AJ .

In practice it is difficult to cool at a rate sufficiently slow to permit equilibrium to be maintained. Thus in solid alloys of the type under consideration the composition of each crystal varies within limits such as are represented by the points P and K in Fig. 112. In a copper-nickel alloy the first formed skeletons of the crystals are rich in nickel and the copper content increases progressively to the last portions to solidify. As already explained, the methods of etching and micro-photography do not permit this gradual variation in composition to be revealed in micrographs. These show the structure as if it consisted of primary skeletons of one constituent in a matrix of another as depicted in Fig. 104 which is a micrograph of a cast copper-nickel alloy containing 50 per cent. of each metal. When, however, solid diffusion does not take place completely during solidification it may be assisted to take place afterwards. If, e.g., an alloy solidifies under such conditions that its crystals vary in composition between P and K (Fig. 112), this variation may be eliminated by maintaining the alloy at a temperature lower than that of V . The time required to produce a uniform distribution of the two metals within each crystal depends on their nature and on the

temperature at which the solid alloy is maintained. When the crystals are made homogeneous by such treatment—which is usually described as annealing—the microstructure of the alloy is similar to that of a pure metal (Fig. 4).

The liquid alloy is a homogeneous solution. At the beginning of solidification minute crystals rich in nickel are formed and the copper content of the melt is increased. This change in the composition of the liquid takes place in the first instance at the points where crystals have begun to grow. Here the melt is enriched with copper and does not become uniform in composition until this copper has diffused throughout it. Throughout the process of solidification the copper content of the melt

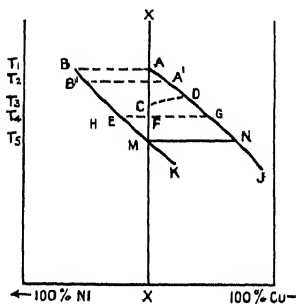


FIG. 113.

is increasing, and as the increase takes place at the surfaces of the growing crystals it tends to produce a concentration gradient in the melt. Diffusion in the liquid tends to eliminate it so that its magnitude depends on the relations between the rate of formation of solid and the rate of diffusion. Diffusion proceeds much more rapidly in the liquid than in the solid, but despite this appreciable concentration gradients are produced in it during rapid cooling. Some of their effects are considered in Part IV in connexion with the solidification of ingots

and castings. For the present they may be neglected as far as solidification is concerned, but it should be mentioned that when one solid solution changes to another the conditions are similar to those realized during solidification, and owing to the slow rate of diffusion in the solid solution that takes the part of the liquid, the gradients described above become very important.

Owing to under-cooling solidification does not begin as soon as the alloy XX is cooled to the point A . Even when the rate of cooling is very slow the liquid cools to a lower temperature before the crystals begin to grow. Thus solidification begins at T_2 instead of at T_1 (Fig. 113). We know that solid of composition B is formed from liquid of composition A at temperature T_1 , and solid of composition B' from liquid of composition A' at T_2 , but we do not know the composition of the solid that is formed from liquid of composition A at temperature T_2 . According to the lines AJ and BK it should not be possible for liquid of composition A to exist at T_2 . When such a condition results from under-cooling these lines do not indicate what solid will be formed, and we can only infer that it will be intermediate in composition between B and B' . In any case when solid begins to form, the composition of the melt moves towards the right and at the same time its temperature rises as a result of the evolution of heat. In consequence of this the composition and temperature of the melt moves in a direction that brings it to

the line AJ at some point between A and A' . Thereafter solidification proceeds according to the lines AJ and BK .

Increase in the rate of cooling exaggerates the effects described above. The amount of under-cooling is increased, and the beginning of solidification is lowered, e.g. to T_3 . Furthermore, heat is abstracted more rapidly while solidification is proceeding, and it is thus more difficult for the liberated heat to raise the temperature of the alloy. Thus, as a result of the formation of solid and the balance between the heat liberated and the heat abstracted, the temperature and composition of the melt moves along a line such as CD (Fig. 113) and reaches AJ at D . Thereafter solidification proceeds in the usual manner.

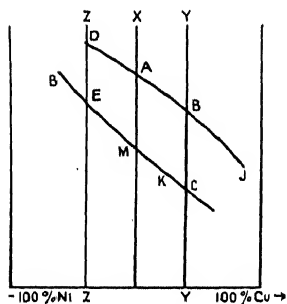
The respective amounts of liquid and solid existing at any temperature in the range of solidification can be determined by the method previously described. Thus, at the temperature T_4 , the amount of liquid is to the amount of solid as EF is to FG . This is only true, however, for equilibrium conditions under which E denotes the average composition of the solid at T_4 . When equilibrium is not attained, the average composition of the solid lies to the left of E , say at H , and the amount of liquid is to the amount of solid as HF is to FG . It follows, therefore, that as the rate of cooling is increased the relative proportions of liquid and solid existing at a given temperature are altered in such a way that the proportion of liquid is increased. This is also shown by Fig. 112 which indicates that an increase in the rate of cooling causes solidification to be spread over a longer temperature range. The explanation is that while the rate of cooling does not influence the deposition of solid along BK it does affect the amount of copper that diffuses from liquid to solid and the amount of solid that is formed in order to counteract the effect of this on the composition of the liquid.

By taking a series of lines such as EFG (Fig. 113) at intervals throughout the range of solidification the amount of solid formed in successive equal temperature intervals under equilibrium conditions may be calculated. When this is done it is seen that the rate of formation of solid becomes smaller as solidification proceeds. The effect is not so marked as in the case illustrated in Fig. 110, and it is influenced by the distance between AJ and BK which varies in different alloys. Nevertheless, at the beginning of solidification the amount of solid formed in each temperature interval is considerable, and as the effect is exaggerated by under-cooling, the beginning of solidification is clearly marked on cooling curves. The end of solidification is, however, difficult to detect.

Liquidus and Solidus.

The essential meaning of the lines AJ and BK in Figs. 112 and 113 is that any point on AJ indicates the composition and temperature of liquid that can exist in equilibrium with solid represented by a horizontally opposite point on BK . Thus liquid of composition A (Fig. 113) can exist in equilibrium with solid of composition B at temperature T_1 ,

and liquid of composition A' can exist in equilibrium with solid of composition B' at temperature T_2 . If liquid of composition A is cooled to T_2 and maintained at that temperature, solid will form. It is not known what the composition of the first formed solid will be, but it will continue to form and change in composition by diffusion from the liquid until the liquid reaches composition A' and the solid is of composition B' . Then no further change will take place at T_2 . Similarly, if the alloy XX is cooled fairly rapidly to T_4 (Fig. 113) so that when this temperature is reached the liquid is of composition G and the solid of average composition H , then diffusion within the solid and from liquid to solid will proceed until the solid is of uniform composition E .



114.

At the temperature T_5 solid of composition M is in equilibrium with liquid of composition N . But M is the composition of the alloy XX , and consequently all the liquid disappears in bringing the solid to this composition. Thus, while the point A on AJ indicates the beginning of solidification the point M on BK indicates its end. These two points can be determined by taking cooling curves while the alloy XX cools at equilibrium rate, but the question arises how are the other points on AJ and BK determined?

In Fig. 114 the lines are shown produced.

Alloy XX begins to solidify at A because at that temperature liquid XX is in equilibrium with solid. Solidification is complete at M because at that temperature solid XX is in equilibrium with liquid and all the liquid disappears in bringing the solid to the requisite composition. Now it is evident that the alloy YY will begin to solidify at B because at that temperature liquid YY can exist in equilibrium with solid, and its solidification will be completed at C because at that temperature solid YY can exist in equilibrium with liquid. The same applies to alloy ZZ which begins to solidify at D and is completely solidified at E . Thus by taking thermal curves of different alloys under equilibrium conditions of cooling any required number of points on AJ and BK can be determined.

With the exception of the above paragraph the foregoing discussion of the solidification of primary solid solutions has been confined to the alloy XX . All that has been said applies, however, to any alloy of this type. The lines AJ and BK when suitably produced represent the equilibrium conditions of solidification for all copper-nickel alloys. The other lines in Fig. 112 have no such general significance. BP and BV apply to the alloy XX cooled at a particular rate. For other alloys, and for XX cooled at other rates, different lines are required. The only point on these lines that can actually be determined is V , the end of solidification during cooling at a particular rate faster than the equilibrium rate.

The line AJ is known as the liquidus of the alloys concerned and under equilibrium conditions represents:

1. The composition of the liquid that can exist in equilibrium with a corresponding solid at a given temperature.
2. The change in the composition of the liquid during the solidification of a given alloy.
3. The temperature at which the solidification of any alloy begins.

The line BK is known as the solidus and under equilibrium conditions represents:

1. The composition of the solid that is deposited from, and can exist in equilibrium with, a corresponding liquid at a given temperature.
2. The average composition of the solid existing at a given temperature, and the change in this during the course of solidification.
3. The temperature at which the solidification of any alloy is completed.

The significance of the liquidus does not alter much with variations in the conditions of cooling except that under-cooling usually prevents solidification beginning as soon as the appropriate point is reached. The basic significance of the solidus is stated in the first paragraph and this does not change with the rate of cooling, but as soon as equilibrium conditions are departed from, the solidus ceases to indicate the features mentioned in the second and third paragraphs. →

ALLOY SYSTEMS (*continued*)

Type 2. The Two Metals are Completely Miscible in the Liquid and Solid State.

Pairs of metals that form alloy systems of this kind may be mixed in any proportions when molten, and when the alloys thus produced solidify, primary solid solutions with the same type of crystal structure as the metals possess are formed. Metals that give an alloy system of this kind must have the same type of crystal structure, but such systems are not
by two same crystal structure.

Thus while copper and gold form systems of this kind, copper and silver do not.

Alloy systems of the type under consideration may be divided into two groups represented respectively by copper-nickel and iron-chromium alloys. The constitutional diagram for the former alloys is shown in Fig. 115 and for the latter in Fig. 116. In both cases the diagram is determined by observing the beginning and end of solidification in a series of alloys as explained in connexion with Fig. 114. Assuming that the rate of cooling used in determining the diagram is slow enough to permit equilibrium to be maintained, the liquidus and solidus curves have the full significance ascribed to them above. In practice, however, alloys are not cooled as slowly as this, and for each alloy cooled at a particular rate we have to assume a diagram like that shown in Fig. 112, i.e. the

range of solidification extends below the solidus and the two metals are not uniformly distributed in each crystal.

All copper-nickel alloys solidify over a range of temperature, and in

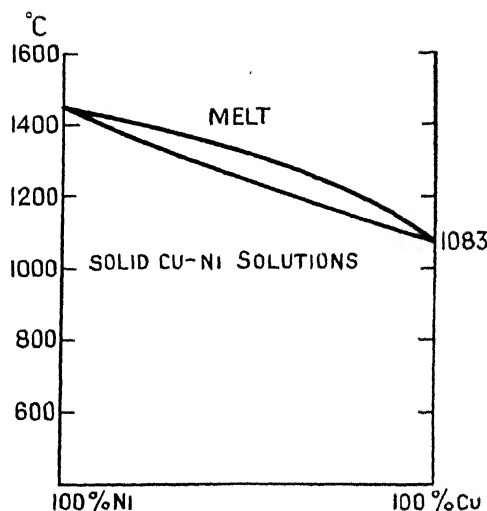


FIG. 115. Cu-Ni alloys.

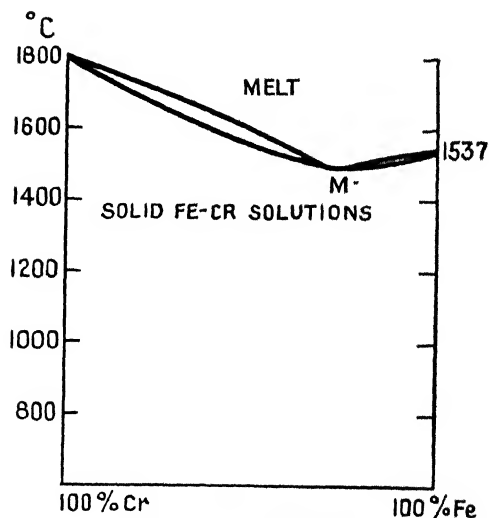


FIG. 116. Fe-Cr alloys.

every case the first solid formed is richer in nickel than the melt. In the iron-chromium system, however, the liquidus and solidus coincide at the minimum point and here the liquid and solid are of the same composition, i.e. there is no selective freezing. In all other alloys selective freezing occurs and the results are similar to those in the copper-nickel

system, except that the first solid formed is rich in iron if the composition of the alloy lies to the right of the minimum and rich in chromium if it lies to the left. Under equilibrium conditions solidification is completed in any alloy when the appropriate point on the solidus is reached, and M does not represent the end of solidification for any alloy except one of this particular composition.

The two face-centred metals copper and nickel form a series of face-centred solid solutions in which the lattice constant varies with the composition, and the two body-centred metals iron and chromium do the same. The lattice constant is not in either case a linear function of the composition, but the deviations from it are not very great.

Type 3. The Two Metals are Completely Miscible when Liquid and Each is Soluble to a Limited Extent in the Other when Solid.

Alloys within the limits of solubility of B in A solidify as solid solutions of B in A while those within the limits of solubility of A in B solidify as solid solutions of A in B . Alloys of intermediate composition solidify as mixtures of the two saturated solid solutions. Alloy systems of the type under consideration may be divided into two groups: (1) in which there is a eutectic, and (2) in which there is a peritectic. The cop an example of the former and the c alloys of the latter. The constitutional diagram for copper-silver alloys is shown in Fig. 117. The freezing-point of copper is lowered by the addition of silver and that of silver by the addition of copper. The two lines representing the lowering of the freezing-points meet at the eutectic point E . In this respect the system resembles the zinc-tin system, but the crystals formed during solidification are solid solutions instead of pure metals and their compositions are given by the lines aS_1 and bS_2 .

The point S_1 represents the limit of solubility of copper in silver. Alloys containing less than 8.8 per cent. of this metal solidify under equilibrium conditions as unsaturated homogeneous silver-rich solid solutions. Thus in the case of the alloy X solidification begins at the point p_1 with the formation of solid of composition c_1 , and the process continues as the temperature falls, the liquid changing in composition from p_1 to p_2 while the solid changes from c_1 to c_2 . Under equilibrium conditions solidification is complete at c_2 . The freezing of an alloy such as Y takes place in a similar way and a copper-rich solid solution is formed.

The alloy Z (Fig. 117) contains more copper than is soluble in solid silver. Solidification begins at the point m with the formation of solid of composition n . As the temperature falls the liquid changes in com-

position along the line mE , while the solid changes along the line nS_1 . At the temperature of the line S_1S_2 solidification is not complete, for whereas the composition of the solid is S_1 that of the alloy is Z . But at this temperature the liquid has attained the composition E , and from this two saturated solid solutions, represented respectively by S_1 and

S_2 , can form. The simultaneous crystallization of these completes the solidification of the alloy. The freezing of alloys of compositions between E and S_2 takes place in a similar way. Solid is first formed along the line bS_2 and the process is completed by the simultaneous formation of two saturated solid solutions at the eutectic point. Under equilibrium conditions alloys to the left of S_1 or to the right of S_2 consist of unsaturated homogeneous solid solutions of the same composition as the alloy. All alloys lying between S_1 and S_2 consist of mixtures in varying proportions of the two saturated solid solutions S_1 and S_2 . As in the zinc-tin system,

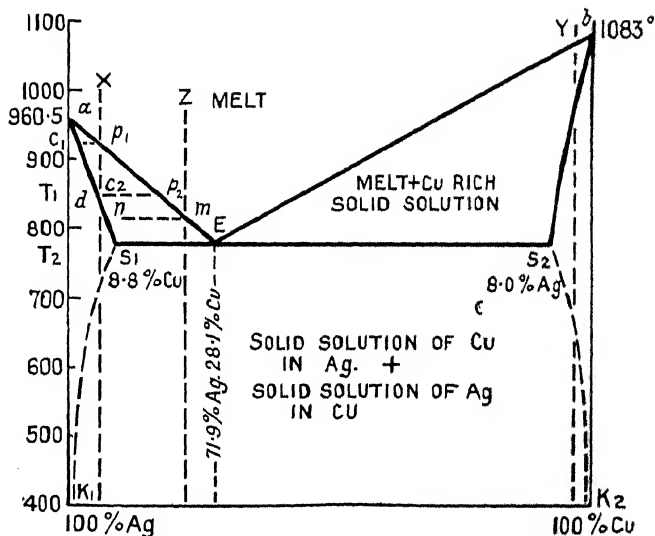


FIG. 117. Cu-Ag alloys.

however, the primary crystals formed before the liquid reaches the point E can be distinguished from the eutectic. Consequently, alloys between S_1 and E consist of the solid solution S_1 plus eutectic—which is itself a mixture of the solid solutions S_1 and S_2 , while those between S_2 and E are composed of the solid solution S_2 plus eutectic.

The effects of accelerated cooling are similar to those described in connexion with the diagram for complete solid solubility. If the rate of cooling through the range of solidification is faster than the equilibrium rate, some eutectic may be formed either in alloys to the left of S_1 or to the right of S_2 . Under equilibrium conditions the solidification of an alloy such as X is completed at C_2 because at this point the average composition of the solid is the same as that of the alloy. When, however, the rate of cooling through the range of solidification is too fast for solid diffusion to maintain a uniform distribution of the solute, the average composition of the solid at the temperature T_1 is not c_2 but d . Freezing, therefore, continues below T_1 , and if the average composition of the solid still lies to the left of X when the temperature T_2 is reached some

liquid will remain. This will be of the eutectic composition, and solidification is therefore completed by the simultaneous formation of the solid solutions S_1 and S_2 . The same holds for alloys to the right of S_2 , so that if the rate of cooling is faster than the equilibrium rate, eutectic will be obtained in alloys which according to the diagram should consist of a single solid solution. Further, in alloys lying between S_1 and S_2 the amount of eutectic will increase with the rate of cooling.

If alloy X is cooled rapidly to a temperature just above the eutectic horizontal $S_1 S_2$ and the temperature is maintained constant, various changes will take place. Solid diffusion will tend to bring about a uniform distribution of copper in the solid. At the same time, as long as liquid remains, copper will diffuse from the liquid to the solid, thus keeping the outer layers of solid at composition S_1 . At the same time more solid of this composition will continue to be deposited, thus keeping the liquid at composition E . Eventually the liquid will disappear leaving crystals which contain 8.8 per cent. of copper at the surface and smaller concentrations in the interior. If the temperature is still maintained constant, solid diffusion will then bring the crystals to the uniform composition c_2 . If, however, the fall in temperature is not interrupted until the alloy has cooled just below $S_1 S_2$, the conditions will be different. In this case the alloy that is maintained at constant temperature contains eutectic instead of liquid. For equilibrium to be established this must disappear and this change takes a very long time.

The structures of alloys of the type under consideration may be inferred from what has been said about the alloy systems Type 1 and Type 2. When alloys containing less than 8.8 per cent. of copper or 8.0 per cent. of silver are cooled at a rate that permits equilibrium conditions to be maintained they consist, when newly solidified, of homogeneous solid solution crystals. Under similar conditions of cooling, alloys that contain from 8.8 to 28.1 per cent. of copper consist of skeleton crystals of the silver-rich solid solution S_1 in a matrix of eutectic, while those that contain from 8.0 to 71.9 per cent. of silver consist of skeleton crystals of the copper-rich solid solution S_2 in a matrix of eutectic. The amount of eutectic increases as the eutectic composition is approached and an alloy of composition E consists entirely of this. When cooling is accelerated several changes in structure are produced. In an alloy of eutectic composition the structure is refined. In alloys that lie between E and S_1 and S_2 respectively the amount of eutectic in a particular alloy increases with the rate of cooling, the eutectic structure becomes finer, and the skeleton crystals exhibit heterogeneity. In alloys that lie to the left of S_1 or the right of S_2 the solid solution crystals exhibit heterogeneity and some eutectic may appear. The amount of eutectic increases with the rate of cooling and decreases as the composition of the alloy approaches pure silver or pure copper respectively.

There are great variations in the extent to which different pairs of metals are soluble in each other when solid, and the different systems so

far discussed may be regarded as belonging to a sequence beginning with zinc-tin alloys and ending with copper-nickel alloys. The mutual solid solubility of zinc and tin is so small that it has not been determined and may from the point of view of the constitutional diagram be neglected. Thus the eutectic horizontal (Fig. 109) is drawn right across the diagram. As the solid solubility of one metal in the other, or of both

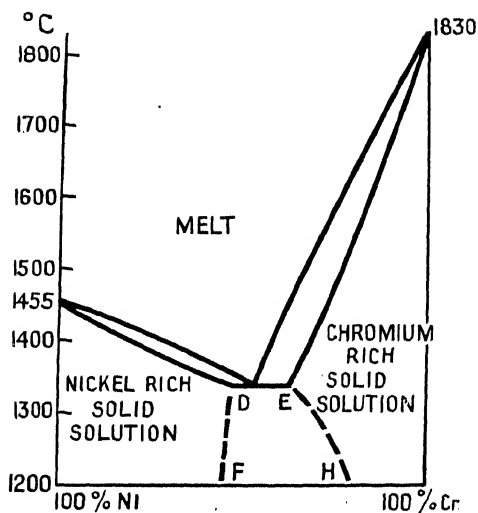


FIG. 118. Ni-Cr alloys.

metals in each other increases, the eutectic horizontal decreases in length as illustrated by the following list:

Zn-Sn alloys.	Zn dissolves 0% Sn.	Sn dissolves 0% Zn.
Al-Si alloys.	Al dissolves 1.65% Si.	Si dissolves 0% Al.
Pb-Sb alloys.	Pb dissolves 2.45% Sb.	Sb dissolves 5% Pb.
Cu-Ag alloys.	Cu dissolves 8% Ag.	Ag dissolves 8.8% Cu.
Pb-Sn alloys.	Pb dissolves 19.5% Sn.	Sn dissolves 2.6% Pb.
Ni-Cr alloys.	Ni dissolves 47% Cr.	Cr dissolves 37% Ni.

The nickel-chromium diagram is shown in Fig. 118. There is some uncertainty about the exact shape of the lines and the position of the points, but it is substantially as indicated. The eutectic horizontal is quite short and the diagram bears a close resemblance to that in Fig. 116. At one time it was considered that the nickel-chromium diagram was of this type, but recent work has shown this to be incorrect. There is an obvious transition from a diagram of the type shown in Fig. 108 through that shown in Fig. 117 to that in Fig. 118, and from Fig. 118 to Fig. 116 and thence to Fig. 115.

When the two metals forming a system of alloys are each soluble in the other to a limited extent there is a range of composition between these limits in which the solid alloys consist of two constituents. In the

systems described above these are formed at the eutectic, and in alloys that are not of eutectic composition the excess constituent crystallizes out before the eutectic temperature is reached. There is, however, another type of system in which alloys within certain limits of composition solidify as two constituents at what is known as a peritectic point. Examples of these are the copper-iron, copper-manganese, thallium-indium, and iron-nickel alloys. The equilibrium diagram of the last-named system will now be considered.

At the temperature of solidification iron has a body-centred cubic lattice and the face-centred nickel dissolves in it up to a certain limit

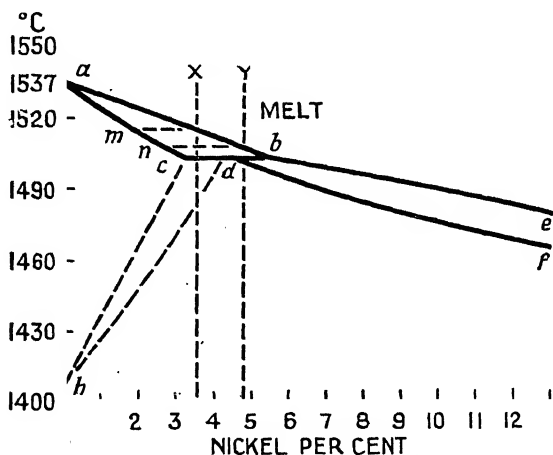


FIG. 119. Portion of Fe-Ni diagram.

forming a primary solid solution. The lines *ab* and *ac* (Fig. 119) are respectively the liquidus and solidus and they show that any alloy that lies to the left of *c* (i.e. that contains less than 3.2 per cent. of nickel) solidifies in this form. In alloys containing more than 5.5 per cent. of nickel solidification begins at the appropriate point on the line *be* (or *be* produced) and the composition of the solid formed is represented by the appropriate point on *df* (or *df* produced). This solid has a face-centred cubic structure and *be* and *df* (which when produced extend right across the diagram to the melting-point of nickel) are respectively the liquidus and solidus for this solid solution. They show that any alloy that contains more than 5.5 per cent. of nickel (i.e. that lies to the right of *b*) solidifies in this form.

c is the upper limit of nickel content of alloys that solidify completely as body-centred solid solutions, and *b* is the lower limit of nickel content of alloys that solidify completely as face-centred solid solutions. In alloys that lie between *c* and *b* both types of solid solution are formed, and in systems of the type under consideration this involves a peritectic change.

The alloys that lie between *c* and *d* must be distinguished from those

that lie between d and b . X is an example of the former and Y of the latter. When X begins to solidify, a body-centred solid solution of composition m is formed. This continues to form as the temperature falls until the liquid reaches b , and under equilibrium conditions the solid is now of composition c . At the exact temperature of the line cdb liquid of composition b may exist in equilibrium with body-centred solid solution of composition c or face-centred solid solution of composition d . Just below this temperature, however, no body-centred solid solution can exist in equilibrium with liquid. Thus, the alloy cannot cool below this temperature until either the liquid or the solid of composition c has disappeared. In the alloy X at the temperature of this line solid of composition d is formed until the liquid disappears. The solid alloy then consists of a mixture of two solid solutions, i.e. body-centred of composition c and face-centred of composition d . The relative amount of each depends on the position of X with respect to c and d , i.e. the constitution alters from 100 per cent. of the former to 100 per cent. of the latter as the nickel content increases from 3.2 to 4.3 per cent. The primary skeletons of the alloy are composed of c and the matrix of d .

When alloy Y begins to freeze body-centred solid solution of composition n is formed. As the temperature falls the liquid moves towards b and the solid changes in composition along nc . At the temperature of the line cdb liquid of composition b reacts with solid of composition c until it changes to composition d and in so doing alters its lattice from the body-centred to the face-centred form. Solidification then proceeds as the temperature falls and solid is formed along the line df until the liquid disappears. In an alloy corresponding exactly to the composition d the reaction between solid c and liquid b proceeds until both these phases disappear and the whole alloy consists of a face-centred solid solution of composition d .

The peritectic point b (Fig. 119) resembles a eutectic point in that at a given temperature one liquid is in equilibrium with two solids. The difference between them is that both liquidus lines rise from a eutectic point while from a peritectic point one rises and the other falls. In all alloys that lie between c and b liquid of composition b is formed at some stage during solidification and the peritectic change takes place at constant temperature until, either (1) the liquid disappears (alloys between c and d), or (2) solid of composition c disappears (alloys between d and b), or (3) both liquid and solid of composition c disappear (the alloy of composition d). The only alloys that contain two constituents when solidified under equilibrium conditions are those that lie between c and d , but under conditions of more rapid cooling two constituents will be formed in alloys over a wider range of composition. Thus in alloys that lie to the left of c some face-centred solid solution may be formed along df during accelerated cooling, and in alloys that lie to the right of d the temperature will be caused to fall below cdb before all the solid of composition c has been transformed by diffusion of nickel from liquid to solid.

The iron-nickel alloys just considered cannot strictly be classified with the thallium-indium and copper-manganese alloys, because the face-centred solid solution formed along *df* is not really a solid solution of iron in nickel. Iron can exist in two crystallographic forms—the body-centred and the face-centred cubic. It solidifies in the body-centred form, and with the body-centred metals chromium and vanadium it can form a continuous series of primary solid solutions (Fig. 116). (It does not do this, however, with the body-centred metals tungsten and molybdenum.) With face-centred metals like nickel and cobalt it cannot form a continuous series of body-centred primary solid solutions, with the consequences shown in Fig. 119. Up to a certain content of nickel or cobalt body-centred solid solutions are formed; above this face-centred solid solutions result, and near the peritectic point these must be regarded as solutions of nickel or cobalt in face-centred iron. As, however, solutions of nickel or cobalt in face-centred iron are continuous with solutions of iron in nickel or cobalt the above distinction makes no difference to the diagram.

FACTORS THAT INFLUENCE SOLID SOLUBILITY

We have seen in the foregoing sections that there are great variations in the extent to which the metals form solid solutions with each other, and the factors which influence this solid solubility may now be considered briefly. Several efforts have been made to correlate solid solubility with other attributes of the metals concerned; the following account is based, however, on the hypotheses advanced by Hume-Rothery in *The Structure of Metals and Alloys* (10).

One of the most important factors affecting the solubility of one metal in another is the relative size of the atoms concerned, and this is not surprising in view of the fact that the crystals of most metals are built up on the basis of close-packing. Although atoms are not small compact spheres, it has been shown that they may be regarded as such for the purpose of considering their packing in metal crystals. Thus the construction of the body-centred cubic, face-centred cubic, and close-packed hexagonal lattices were described in Chapter II by considering various ways of packing spheres. In such arrangements the shortest distance between two atomic centres may be taken as the diameter of the atoms concerned. In the body-centred cubic lattice (Fig. 5) the shortest distance between atomic centres is along the cube-diagonal and each atom has eight close neighbours at a distance of $\frac{a\sqrt{3}}{2}$, where a is the lattice constant. In the face-centred cubic lattice (Fig. 6) the shortest distance between atomic centres is along the cube-face diagonal and each atom has twelve close neighbours at a distance of $\frac{a\sqrt{2}}{2}$. When the close-packed hexagonal lattice is built up as described in Chapter II

and shown in Fig. 6, each atom has twelve close neighbours at distance a . In such a lattice the axial ratio $c/a = 1.633$. If, however, the axial ratio is greater or less than this, then the six closest neighbours on the same basal plane will be situated at a different distance from the other six, three of which lie on the basal plane above and three on the basal plane below.

The atomic diameter of an atom is not, however, a constant independent of the atomic binding forces in the crystal, and different diameters have to be assigned to the same atom when present in ionic, homopolar, and metallic crystals respectively. Even in different types of metallic crystals the atomic diameter varies, and the diameter obtained from the closest distance of approach of the atoms in a body-centred crystal will not be the same as the effective diameter of these atoms when in solid solution in a face-centred crystal. In this connexion it is the co-ordination number, i.e. the number of immediate equidistant neighbours, that has to be taken into account, and when atoms of a body-centred metal are dissolved in a face-centred one their diameter has to be corrected to allow for the change in co-ordination number. In general, the atomic diameter diminishes with the co-ordination number and if d is the diameter of an atom of a face-centred cubic metal (co-ordination number 12) it must be decreased by 3 per cent. if the atom is incorporated in a body-centred cubic-lattice (co-ordination number 8).

In studying the effect of the atomic diameter on the mutual solid solubility of metals, the diameters of atoms which form face-centred cubic or close-packed hexagonal crystals may be deduced directly from the distances of closest approach in the crystals of the elements. Values obtained in this way may also be used for atoms which form body-centred cubic, close-packed hexagonal in which the axial ratio is not 1.633, and other types of lattice. Alternatively, the values obtained in this way may be corrected in order to allow for the difference in co-ordination number between these lattices and face-centred lattices respectively. (Thus the diameters obtained from the closest approach of the atoms in a body-centred metal may be multiplied by 1.03 to allow for the 3 per cent. difference in diameter between lattices with co-ordination numbers of 8 and 12 respectively. Alternatively, the diameter of an atom of a body-centred cubic metal when present in a face-centred cubic lattice may be calculated from the structure of alloys. Values of the atomic diameter obtained from the distances of closest approach are tabulated by Hume-Rothery, who also gives the corrected values for the atoms of elements that do not form face-centred cubic or close-packed hexagonal lattices.

In a survey of the primary solid solutions of a number of metals in copper and silver, Hume-Rothery, Mabbott, and Channel-Evans observed that when the atomic diameters of the solvent and solute atoms differed by more than about 14–15 per cent. of the diameter of the solvent, the

extent of solid solubility was very restricted, whereas, when the difference in atomic diameters was less than this, solid solubility might be considerable. Thus when the atomic diameters differed by more than 14–15 per cent. of the diameter of the solvent, the 'size-factor' was said to be unfavourable for the formation of solid solutions; while, when the difference was less, the 'size-factor' was said to be favourable. For this purpose the diameters considered were those obtained from the closest distances of approach in the crystals of the elements, and corrections for changes in co-ordination number were not applied. We have already seen, however, that the diameter of the same atom is different in ionic and metallic crystals respectively, and in Chapter II it has been explained that in the crystals of aluminium, thallium, lead, indium, and β -tin, the atoms are incompletely ionized. Should these atoms be more fully ionized in the crystals of alloys, the atomic diameters obtained from consideration of the crystals of the elements will not be maintained. It appears, for example, that when indium is dissolved in silver the atom is completely ionized. In studying the solubility of these metals in copper and silver it was assumed that they would be completely ionized and approximate corrections were applied to allow for the decrease in atomic diameter that would result from this.

A survey of the solid solutions in magnesium suggests that the same principle of size-factor can be applied, and data for solid solutions in iron also appear to support this hypothesis. In all this work the favourable size factor has been assumed to be limited by a difference of 14 per cent., but this value is arbitrary and may require modification in some cases. It is not certain that an atom can be assigned a diameter which is really independent of the valency and crystal structure of the metal in which it forms a solid solution, and difficulty arises with elements which may change their state of ionization on entering into solid solution. (There is little doubt, however, that the size-factor is the first characteristic to be considered in order to decide whether two elements are likely to form solid solutions or not.)

The size-factor indicates which elements are likely to be soluble to a considerable extent in a given metal, and it remains to consider the other factors which may prevent the formation of a wide range of solid solutions even when the size-factor is favourable. [One of these is the tendency to form intermediate constituents.] As explained in the next section, certain pairs of metals can combine in certain definite proportions to form crystals with a different structure from that of either of the pure metals. These crystals are known as intermediate constituents, and if the two metals concerned have a strong tendency to form such constituents the range of solid solubility is likely to be restricted. Generally speaking the more electronegative the solute element and the more electropositive the solvent (or vice versa), the greater is the tendency to form intermediate constituents. Electropositive elements are those lying towards the left in Table 13, while

electronegative elements are those lying towards the right. Sulphur, selenium, and tellurium are strongly electronegative and readily form compounds with the normal metals, and consequently the solid solubility of these in the normal metals is usually, if not always, very restricted. In the group silicon, germanium, tin, and lead the electronegative character is much less marked and these elements are able to enter into solid solution in some metals to quite an appreciable extent when the size-factor is favourable. Thus copper can dissolve in solid solution 14 per cent. of silicon and 12 per cent. of germanium.

The next point to be considered is whether the tendency for two metals to form solid solutions is necessarily reciprocal, and here a survey of the data indicates that other things being equal a metal of lower valency is more likely to dissolve one of higher valency than vice versa. Thus copper can dissolve 14.0 per cent. of silicon, while silicon dissolves less than 2 per cent. of copper; silver can dissolve 12.2 per cent. of tin, while tin dissolves less than 0.1 per cent. of silver; and copper can dissolve 38.4 per cent. of zinc, while zinc dissolves 2.3 per cent. of copper.

We have now seen that, even when the size-factor is favourable, the extent to which one metal is soluble in another may be restricted by the tendency to form intermediate constituents, or by the fact that a metal of lower valency is not readily soluble in one of higher valency. It remains now to consider the extent of solid solubility obtained when the size-factor is favourable, the tendency to form intermediate constituents is not strong and the solute metal has not a lower valency than the solvent. In this case the limit of solid solubility is influenced by the fact that the extent to which the number of electrons in the lattice may be increased is restricted. From this it follows (1) that when other things are equal the most extensive ranges of solid solubility will be obtained when the two elements concerned have the same valency, and (2) that the range will decrease as the valency of the solute increases above that of the solvent. Thus, in the following pairs of metals, both have the same valency and they are mutually soluble in each other in all proportions: K-Rb, Ag-Au, Cu-Au, As-Sb, Sb-Bi, Mo-W, Ni-Pd, Ni-Pt, Pd-Pt. The formation of continuous solid solutions is not confined to cases where the two metals have the same valency, but occurs also in many binary alloys of the transition elements with one another and with copper, silver, and gold, e.g. Fe-Cr, Ni-Cu, Cu-Pt, when the size-factor is favourable. The transition elements, however, are of variable valency, and since their degrees of ionization in the metal are not always known, it is impossible to say whether complete miscibility in the solid is restricted to pairs of metals of equal valency or whether a continuous change can take place from a univalent to a divalent metal provided that the crystal structures are the same.)

It remains to consider the diminution of solid solubility when the valency of the solute element increases above that of the solvent. If an

atom of a divalent element is incorporated in the lattice of the univalent metals copper or silver, the number of electrons is increased by one. The substitution of an atom of a trivalent element will introduce two extra electrons, while a tetravalent element will introduce three extra electrons. If, therefore, there is a limit to the extent to which extra electrons may be introduced, the solubilities of divalent, trivalent, and tetravalent elements in copper and silver should be in the atomic proportions of $1 : \frac{1}{2} : \frac{1}{3}$, except in so far as the solubility is affected by other factors. From the work of Hume-Rothery, Mabbott, and Channel-Evans it is seen that the solubilities of the divalent metals zinc and cadmium in copper and silver are approximately 40 atomic per cent. except in the case of cadmium in copper where the size-factor is unfavourable. Similarly, in the case of the trivalent elements, aluminium, gallium, and indium the solubilities are approximately 20 atomic per cent. except in the copper-indium alloys where the size-factor is unfavourable. Finally, the solubilities of the tetravalent metals silicon and germanium in copper and of tin in silver are of the order of 13 atomic per cent. Thus it appears that in so far as the solid solutions of the above-mentioned metals in copper and silver are concerned the limit of solid solubility is reached when the electron concentration is increased by 40 per cent. In the univalent basis metals there are one hundred electrons per hundred atoms, i.e. the electron concentration is 1. The replacement of forty univalent atoms by an equal number of divalent atoms increases the number of electrons to 140, i.e. the electron concentration is raised to 1.4. The same result is obtained by replacing 20 univalent atoms by an equal number of trivalent atoms or by replacing 13.3 univalent atoms by an equal number of tetravalent atoms. Thus, in so far as the present examples are concerned, the limit of solid solubility may be said to be reached when the electron concentration is raised from 1 to 1.4.

INTERMEDIATE CONSTITUENTS

In the binary alloy systems previously considered we have been dealing with the consequences that arise from differences in the solid solubility of the two metals concerned. When these are completely insoluble in each other, all alloys contain crystals of both metals. When they are completely soluble in each other, all alloys consist of a primary solid solution. When they are partially soluble in each other, alloys at the ends of the system consist of a primary solid solution while intermediate alloys consist of two primary solid solutions. In many alloy systems, however, additional constituents are formed, and as the composition of these is intermediate between those of the primary solid solutions at the ends of the systems they may be termed intermediate constituents.

The formation of these depends on the fact that the atoms of certain pairs of metals can combine in certain definite proportions to form

crystals that have a different crystal structure and different properties from those of the pure metals. When a primary solid solution is formed, the lattice constant is altered progressively as the proportion of the solute element is increased, and this is accompanied by a gradual change in properties. In all primary solid solutions the crystal structure and properties are clearly modifications of those of the basis metal. In intermediate constituents, however, this is not generally the case, and sometimes the contrast is very pronounced. Thus the two ductile face-centred cubic metals copper and aluminium combine in the proportions of one atom of copper to two of aluminium (i.e. 54 per cent. Cu and 46 per cent. Al by weight) to form a hard and brittle intermediate constituent which has a tetragonal space-lattice ($a : 6.054 \text{ \AA.}$ and $c = 4.864 \text{ \AA.}$) with 12 atoms (4 Cu and 8 Al) per unit cell. Not all intermediate constituents are, however, so strikingly different from the constituent metals as this one, and that formed by copper and zinc in equal atomic proportions exhibits properties of the same order as the primary solid solution of zinc in copper. As intermediate constituents are formed by the combination of the atoms of certain pairs of metals in definite proportions, their composition may be expressed conveniently by means of a chemical formula, e.g. CuAl_2 and CuZn in the case of the constituents mentioned above. It is customary, in fact, to describe some or all of these constituents as intermetallic compounds.

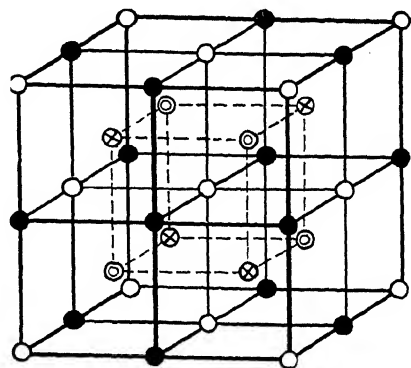
In the numerous alloy systems that have been studied a very large number of intermediate constituents have been recognized and the variations in properties exhibited by them are considerable. At the one extreme there are constituents, e.g. CuZn , AuZn , AgCd , Cu_3Al , &c., which (1) have mechanical properties similar to primary solid solutions, (2) form crystals with cubic structures that grow by developing skeletons and filling the interstices, and (3) dissolve in solid solution appreciable amounts of either of the component metals. At the other there are constituents, e.g. CuAl_2 , Fe_3W_2 , FeAl_3 , &c., which (1) are very hard and brittle, (2) form crystals with more complex structures that do not grow by developing skeletons, and (3) do not dissolve either of the component metals in solid solution. Between these extremes there are constituents which exhibit various combinations of the characteristics mentioned above, and in addition there is another type in which one of the components is not a metal, e.g. the carbides and nitrides which are extremely hard and brittle, and strikingly different in many ways from primary solid solutions or constituents of the CuZn type. The great variety of properties obtainable in modern alloys is to a large extent due to the existence of these substances, for whereas all the common industrial metals are comparatively soft when pure, and primary solid solutions based on them are not very much harder, intermediate constituents of great hardness can be obtained when desired.

From the point of view of the factors that control their composition and crystal structure three different kinds of intermediate constituents

may be distinguished namely, electron compounds, normal valency compounds, and size-factor compounds. The first type is the most important from the point of view of the kind of alloys with which this book is particularly concerned and may be dealt with first.

Electron Compounds.

Crystals of organic and inorganic compounds are built up of two or more different kinds of atoms in definite atomic proportions. Crystals of intermediate metallic constituents are similar in this respect. In crystals of compounds, however, the different kinds of atoms occupy definite positions in the structure, whereas in intermediate constituents this condition does not necessarily obtain. In Fig. 24 the space-lattice of sodium chloride is shown, and it will be seen that the two kinds of atoms are disposed in an orderly manner on a common space-lattice. Taken together the two kinds of atoms form a simple cubic lattice, and if either kind could be taken away without displacing the others, these would remain on a face-centred cubic lattice. This kind



○ A ⊗ C
● B ⊙ D
FIG. 120.

of orderly distribution of the various sorts of atoms is characteristic of all organic and inorganic compounds, but is not always found in intermediate metallic constituents. The alternative arrangement is known as random or statistical, i.e. in any small portion of a crystal the two sorts of atoms are present in the requisite proportions, but there is no order in the way in which they are distributed among the lattice points. If either kind of atoms could be taken away without disturbing the others, the remainder would not form a regular pattern in space.

All the lattice points in Fig. 120 form a body-centred cubic lattice. The *A* and *B* points taken together form a simple cubic lattice and the *C* and *D* together another simple cubic lattice. *A*, *B*, *C*, or *D* points taken separately form face-centred cubic lattices. Thus the lattice shown may be described as one body-centred cubic, two interpenetrating simple cubic, or four interpenetrating face-centred cubic lattices. If two sorts of atoms in equal proportions combine to form a lattice of this kind, an ordered arrangement will result if one sort occupies all the *A* and *B* positions and the other all the *C* and *D* positions. If, however, some atoms of each sort are found in *A*, *B*, *C*, and *D* positions, then the

arrangement is random. Similarly, if two sorts of atoms in the proportions of 3 atoms of one to 1 of the other combine to form a lattice of this kind, an ordered arrangement will result if the atoms present in the smaller proportions are all situated at *A*, *B*, *C*, or *D* positions. If, however, some of these atoms are found in *A*, *B*, *C*, and *D* positions the arrangement is random.

The constituent formed by copper and zinc atoms in equal proportions (CuZn) has a body-centred cubic lattice, and below 460°C . all the *A* and *B* positions (Fig. 120) are occupied by copper atoms while all the *C* and *D* positions are occupied by zinc atoms. The same applies to a number of other constituents formed in alloys between copper, silver, and gold on the one hand and zinc and cadmium on the other, e.g. AgZn , AuCd , &c. In all these the metals are present in equal atomic proportions, the lattice is body-centred cubic, the *A* and *B* positions are occupied by atoms of one kind and the *C* and *D* positions by those of the other. Copper and aluminium in the proportions Cu_3Al form a constituent with a body-centred cubic lattice and properties similar to those of CuZn , &c. In this case all the *A*, *B*, and *C* positions are occupied by copper atoms and the *D* positions by aluminium. Copper and tin in the proportions Cu_3Sn also form a constituent with a body-centred cubic lattice, but in this case the relative numbers of the atoms do not permit of an ordered distribution among the lattice points. The two sorts of atoms are therefore distributed at random in such a way that in any small portion of a crystal they are present in the requisite proportions but each sort is disposed indiscriminately at *A*, *B*, *C*, and *D* points.

Of the four elements in the series vanadium, chromium, manganese, and α -iron (see Table 11), all have a body-centred cubic lattice except manganese. This suggests some similarity between the manganese lattices and the body-centred cubic lattice, and this is confirmed by the fact that several constituents have been found which resemble those described above and yet have the same kind of lattice as β -manganese. This lattice is cubic with 20 atoms per unit cell and the same kind of lattice is formed by Ag_3Al , Cu_5Si , and Au_3Al . The X-ray reflections indicate that the two sorts of atoms are distributed at random among the lattice points, and in the case of Cu_5Si a random distribution is suggested by the atomic proportions.

Another type of constituent of frequent occurrence is that formed by copper and zinc in the proportions Cu_5Zn_8 . This constituent has a complicated lattice and its derivation from a body-centred cubic lattice is shown in Fig. 121. All the lattice points in the upper portion of this figure form a body-centred cubic lattice, and five different kinds of points are represented by black squares, white squares, black circles, white circles, and crossed circles. The complete drawing includes 27 unit body-centred cubes ($3 \times 3 \times 3$). The structure of Cu_5Zn_8 shown at the bottom of Fig. 121 is derived from this by the elimination of the lattice points represented by the crossed circles and the shifting of the remaining

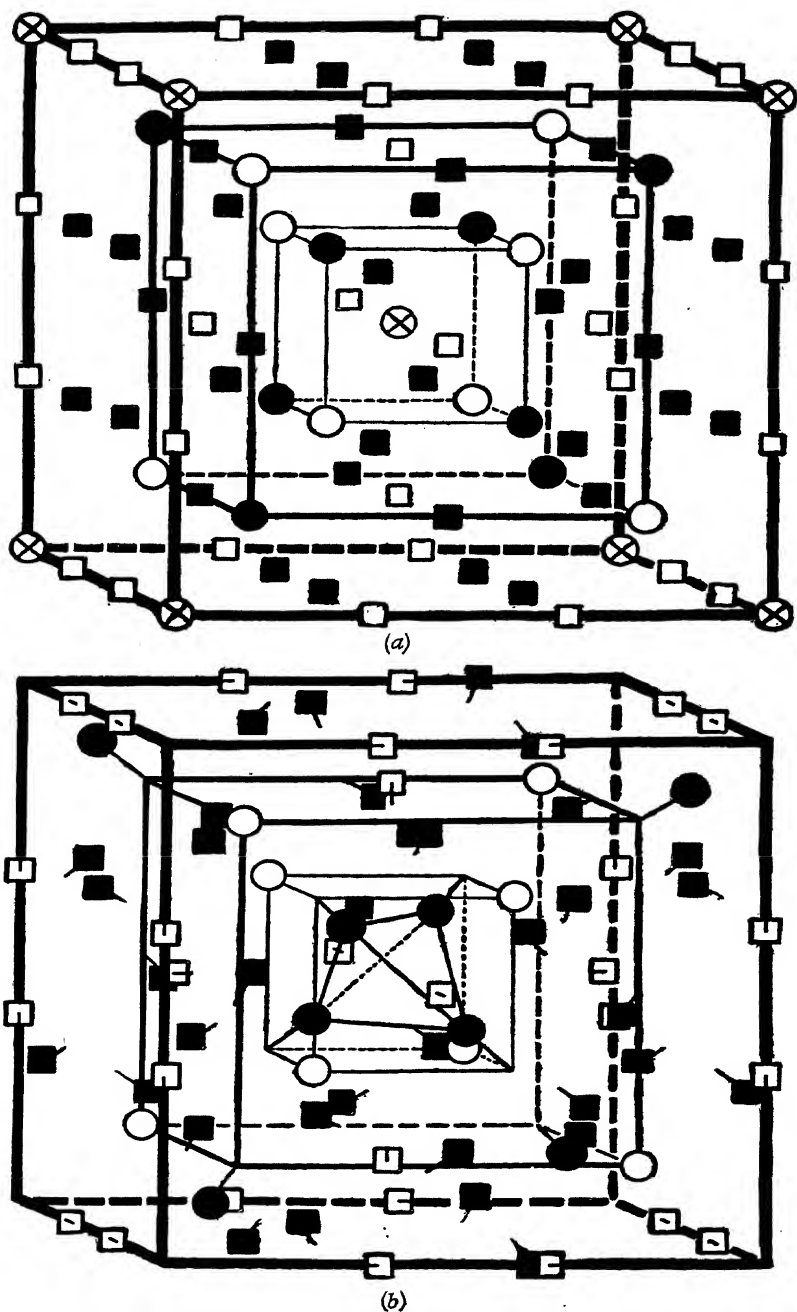


FIG. 121. Showing the derivation of the structure of γ -brass (Cu_5Zn_8), lower figure, from a body-centred cubic arrangement, upper figure. (From Bragg, *The Crystalline State*. Original from Bradley and Thewlis, *Proc. Royal Soc. A*, 112, 1926.)

points in order to fill up the gaps. As each of the lattice points represented by the crossed circles at the corners of the large cube is shared by the 8 similar cubes meeting at this point, and as the point represented by the crossed circle in the centre of the cube belongs entirely to that cube, the elimination of all the points represented by crossed circles means the elimination of 2 atoms per cube. The structure of Cu_5Zn_8 is thus derived from a body-centred cubic lattice by the elimination of 2 atoms from each block of 27 unit body-centred cubes and the displacement of the remaining atoms to fill the spaces. As a result of this the unit of structure is the large cube derived from 27 small cubes and containing 52 atoms. As the distribution of the atoms around each point from which an atom has been eliminated is the same throughout the lattice, the structure of Cu_5Zn_8 may also be described as a body-centred lattice with 26 atoms clustered around each of the lattice points indicated by the crossed circles in the top part of Fig. 121.

In the crystals of Cu_5Zn_8 every cluster of 26 atoms is identical and consists of four sets of structurally equivalent atoms, viz. 4 *A* atoms represented by white circles in Fig. 121 (bottom), 4 *B* atoms represented by black circles, 6 *C* atoms represented by white squares, and 12 *D* atoms represented by black squares. The atoms of this compound are distributed in an orderly manner among the lattice points so that copper atoms occupy the 10 *B* and *C* positions and zinc atoms the 16 *A* and *D* positions. A number of other constituents containing the same proportions of atoms, e.g. Cu_5Cd_8 , Ag_5Zn_8 , Ag_5Cd_8 , Au_5Zn_8 , and Au_5Cd_8 form crystals with the same space-lattice as Cu_5Zn_8 . In some of these, e.g. Ag_5Zn_8 and Au_5Zn_8 , the two sorts of atoms are distributed among the lattice points in the same ordered manner as above. In others, however, the distribution is not so completely ordered, e.g. in Cu_5Cd_8 . Other constituents that form similar space-lattices are Cu_5Al_4 , Cu_5Ga_4 , $\text{Fe}_5\text{Zn}_{21}$, $\text{Co}_5\text{Zn}_{21}$, $\text{Ni}_5\text{Zn}_{21}$, $\text{Pd}_5\text{Zn}_{21}$, $\text{Pt}_5\text{Zn}_{21}$, $\text{Cu}_{31}\text{Sn}_8$. In all these except $\text{Cu}_{31}\text{Sn}_8$ the total number of atoms in the unit is either 13 or 26 so that either two units or one unit will be situated at each lattice point, but the relative proportions of atoms, viz. 9 : 4 and 5 : 21, does not suggest an ordered distribution among the *A*, *B*, *C*, and *D* positions (Fig. 121).

It is evident from the above that many intermediate constituents can be classified according to their crystal structure. It is also clear that the formation of a particular structure does not depend on the relative proportions of the two sorts of atoms for CuZn , Cu_3Al , and Cu_5Sn have the same structure, Ag_3Al and Cu_5Si have the same structure, and Cu_5Zn_8 , Cu_5Al_4 , and $\text{Fe}_5\text{Zn}_{21}$ have the same structure. Furthermore, it does not depend on the suitability of a particular structure for an ordered distribution of the two sorts of atoms. Thus, while CuZn and Cu_3Al exhibit ordered distributions on the body-centred lattice (Fig. 120), Cu_5Sn has a random distribution and Ag_3Al and Cu_5Si have random distributions in the β -manganese lattice. Similarly, on the complex cubic lattice

described, Cu_5Zn_8 has an ordered distribution, while Cu_5Cd_8 , $\text{Fe}_5\text{Zn}_{21}$, &c. have not. The case is quite different from that which obtains in crystals of chemical compounds and it is clear that the formation of these intermediate constituents depends on other factors. These have been recognized by Hume-Rothery, who found that the formation of a particular type of crystal structure depends on a certain ratio between the numbers of atoms and the number of valency electrons. This is now known as Hume-Rothery's Law and some of its applications will be considered.

The formation of the body-centred cubic structure typified by CuZn depends on a ratio of 3 valency electrons to 2 atoms, and reference to Table 11 will show that copper, silver, and gold have each 1 valency electron, zinc and cadmium have 2, aluminium has 3, and tin has 4. Thus, CuZn , CuCd , AgZn , AuCd , &c., Cu_3Al , and Cu_3Sn all give the required ratio. The formation of the β -manganese structure depends on the same ratio, and as silicon has 4 atoms Ag_3Al , Cu_5Si , and Au_3Al satisfy the ratio. The formation of the complex cubic lattice typified by Cu_5Zn_8 depends on a ratio of 21 valency electrons to 13 atoms and this is satisfied by Cu_5Zn_8 , Ag_5Zn_8 , Au_5Cd_8 , &c., by Cu_9Al_4 , and by $\text{Cu}_{31}\text{Sn}_8$. The constituents NiAl , CoAl , MnAl , and FeAl all have the same type of space-lattice as CuZn . Aluminium has 3 valency electrons and if the 3 : 2 rule holds for these constituents it means that for some reason the transition elements function as if they had no valency electrons. If the valency of transition elements in constituents of this kind can be assumed to be zero, the compositions of constituents with the Cu_5Zn_8 structure may be calculated. The ratio for this is 21 electrons to 13 atoms which is satisfied by $\text{Fe}_5\text{Zn}_{21}$ (42 electrons from the zinc and 26 atoms). Constituents formed by the transition elements Fe, Co, Ni, Pd, Pt, &c., with Zn and Cd, e.g. $\text{Fe}_5\text{Zn}_{21}$, $\text{Co}_5\text{Zn}_{21}$, $\text{Ni}_5\text{Cd}_{21}$, &c., have been studied and found to have this lattice.

In the alloys of copper, silver, and gold on the one hand with zinc and cadmium on the other a third type of constituent with a close-packed hexagonal structure and corresponding to the composition CuZn_3 , AgCd_3 , AuZn_3 &c., is formed. At this composition the electron : atom ratio is 7 : 4 and constituents with a similar structure are formed in other systems when this ratio is realized i.e. Cu_3Sn , Cu_3Ge , Cu_3Si , Ag_3Sn , Ag_3Al_3 , Au_3Al_3 , Au_3Sn . The various types of electron compounds at present recognized and the constituents of each type may be tabulated as follows:

Electron : Atom Ratio = 3 : 2

Body-centred Cubic Structure

CuBe , CuZn , AgMg , AgZn , AgCd , AuZn , AuCd , Cu_3Al , Cu_3Ga , Cu_3Sn , CoAl , NiAl , FeAl .

β -Manganese Structure

Ag_3Al , Au_3Al , Cu_5Si , CoZn_3 .

Electron : Atom Ratio = 21 : 13

γ -Brass Structure

Cu_5Zn_8 , Cu_5Cd_8 , Cu_9Al_4 , Cu_9Ga_4 , Cu_9In_4 , $\text{Cu}_{31}\text{Si}_8$, $\text{Cu}_{31}\text{Sn}_8$, $\text{Fe}_5\text{Zn}_{21}$, $\text{Co}_5\text{Zn}_{21}$, $\text{Ni}_5\text{Zn}_{21}$, $\text{Rh}_5\text{Zn}_{21}$, $\text{Pd}_5\text{Zn}_{21}$, $\text{Pt}_5\text{Zn}_{21}$, $\text{Ni}_5\text{Cd}_{21}$, Ag_5Zn_8 , Au_5Zn_8 .

Electron : Atom Ratio = 7 : 4

Close-packed Hexagonal Structure

CuZn_3 , CuCd_3 , Cu_3Sn , Cu_3Ge , Cu_3Si , AgZn_3 , AgCd_3 , Ag_3Sn , Ag_3Al , Au_5Al_3 , AuZn_3 , AuCd_3 , Au_3Sn .

It is thus clear that the formation of electron compounds depends on the ratio of valency electrons to atoms and not on the relative proportions of the different kinds of atoms or their distribution among the lattice points. This is in accordance with the nature of metallic crystals, which as explained in Chapter II consist of a lattice of ions and free electrons and thus differ from other crystals in which electrons are exchanged or shared. A large amount of painstaking work has been required to determine the composition and crystal structure of these constituents and in some cases to find out the distribution of the two sorts of atoms on a common lattice. Many investigators have taken part in the work, conspicuous among whom have been A. Westgren and A. J. Bradley, not only in connexion with the subject just considered but with all aspects of the study of alloys by means of X-rays.

Normal Valency Compounds.

The electron compounds considered above resemble the normal compounds of inorganic chemistry in that they are composed of two sorts of atoms in certain proportions, they differ from these, however, in that (1) the two sorts of atoms are not necessarily distributed symmetrically on the lattice points, (2) the type of lattice formed is not directly related to the relative proportions of the two kinds of atoms, and (3) the relative proportions of the atoms are not determined by the valency laws that apply to the formation of ionic and homopolar crystals. The normal valency compounds now to be considered have a much closer resemblance to ordinary inorganic compounds.

As explained in Chapter II the formation of inorganic compounds depends on the exchange or sharing of electrons, and two different types are distinguished, namely, ionic and homopolar compounds. In those of the former class the more electropositive element detaches its valency electrons and the more electronegative element attaches them so as to bring its number of valency electrons up to eight. For the formation of such compounds the atoms must be present in such proportions that the number of electrons detached by the electropositive element is equal to the number required by the electronegative element. Thus one atom of sodium (one valency electron) combines

with one of chlorine (seven valency electrons), one atom of calcium (two valency electrons) combines with two of fluorine (seven valency electrons), and one atom of zinc (two valency electrons) combines with one of sulphur (six valency electrons). The characteristic feature of homopolar crystals is that the number of neighbours of each atom is equal to eight minus the number of valency atoms in the structure of that atom.

In inorganic compounds the relative proportions of the two kinds of atoms are controlled by the number of valency electrons in the structure to these atoms. The most typical ionic compounds are formed between the metals on the left of Table 12, which have small numbers of valency electrons that are readily detached, and the non-metals on the right, which only require one or two electrons to complete their valency group of eight. The elements in the middle of Table 12, with four, five, and six valency electrons are intermediate in properties between the strongly electropositive elements and the strongly electronegative elements, and the metals in this range are capable of acting in a similar way to non-metals in their combinations with more electropositive metals. The metals concerned are germanium, tin, and lead with four electrons, arsenic, antimony, and bismuth with five, and selenium and tellurium with six. These metals combine with more electropositive metals to form normal valency compounds.

The electropositive metal magnesium (two valency electrons) combines with germanium to form the normal valency compound Mg_2Ge , and similar compounds are formed with tin and lead. It also combines with arsenic to form the normal valency compound Mg_3As_2 in which the six electrons detached by the three magnesium atoms are able to complete the eights in the two arsenic atoms which have five electrons. Similar compounds are formed with antimony and bismuth, and with selenium and tellurium compounds of the type MgSe are produced.

Compounds of this last type (MgSe) have the same kind of space-lattice as sodium-chloride (NaCl) Fig. 24, and other compounds which have ionic crystal structures of this type are formed between calcium, strontium, barium, tin, and lead on the one hand and selenium and tellurium on the other. Compounds of the type Mg_2Ge have a calcium fluoride structure. This can be illustrated by reference to Fig. 9 showing the tetrahedral cubic structure. This lattice consists of two interpenetrating face-centred cubic lattices represented by the black and white spots respectively, and in its structure there are an equal number of each kind of lattice points. The face-centred cube formed by the black spots is divided into eight smaller cubes in Fig. 9 and the white spots are situated in the middle of four of them. If, however, another set of white spots is placed in the middle of the other four little cubes, the lattice consists of three interpenetrating face-centred cubic lattices and there are twice as many white spots as black ones. This is the kind of structure obtained in calcium fluoride (CaF_2), and all the points

represented by black spots are occupied by calcium atoms while those represented by white spots are occupied by fluorine atoms. In Mg_2Ge the white spots are occupied by magnesium atoms and all the black ones by germanium atoms. Other compounds of this type are Mg_2Si , Mg_2Sn , Mg_2Pb , and Cu_2Se .

It remains to consider normal valency compounds of homopolar type. We have seen in Chapter II that the elements carbon (diamond), silicon, germanium, and β -tin form homopolar crystals with the tetrahedral cubic lattice shown in Fig. 9. In this lattice each atom indicated by a white spot has four neighbours indicated by black spots, and each atom indicated by a black spot has four neighbours indicated by white spots. As the elements concerned have each four valency electrons the homopolar crystal is linked up by each atom sharing one electron with each of its four neighbours. For the formation of such a crystal there must be a ratio of four electrons to every atom, but it is not necessary for each atom to provide an equal number of electrons. Thus the structure may be formed by two different kinds of atoms when one of them has more than four electrons and the other the same number less than four. Aluminium, for example, with three electrons combines with antimony (5 electrons) to form the compound AlSb which has a homopolar tetrahedral cubic structure. Other compounds of the same kind are formed by the divalent metals beryllium, zinc, cadmium, and mercury on the one hand and the elements sulphur, selenium, and tellurium (with 6 electrons) on the other, and also by the trivalent metals aluminium and gallium on the one hand and phosphorus, arsenic, and antimony (with 5 electrons) on the other.

Size-factor Compounds.

Primary solid solutions of the interstitial type are formed when the atomic diameter of the solute is very much smaller than that of the solvent. In the same way some of the intermediate constituents in alloys containing an element with a small atomic diameter have crystal structures in which the smaller atoms fit into the spaces between the larger atoms. The elements chiefly concerned are hydrogen, nitrogen, carbon, and boron, and many of their compounds, particularly those of carbon and nitrogen are of great interest because of their great hardness and high melting-points. One method of constructing an interstitial structure based on a face-centred cubic lattice is shown in Fig. 9 (diamond structure), and another type may be obtained by placing another set of atoms in the centres of the other four little cubes into which the large face-centred cube is divided (calcium fluoride structure). Still another type may be obtained by placing interstitial atoms in the middle of the edges of the large face-centred cube instead of in the interior, and corresponding interstitial structures may be based on the close-packed hexagonal and body-centred cubic lattices. When we know the diameter of the larger atoms, the spaces available for the smaller ones

may be calculated, and if the atomic diameters of the smaller atoms are too large to be accommodated without distortion of the lattice, an interstitial structure may still be formed in which the basic, cubic, or hexagonal symmetry is to some extent destroyed. A number of compounds of this type has been studied, and it appears that the relative positions of the two kinds of atoms and the proportions in which they are present are determined by their respective atomic diameters. Some of the resulting structures are, however, rather complicated and for fuller information reference must be made to *The Structure of Metals and Alloys* (10) and the references given there.

Intermediate Constituents and Solubility.

In this section attention is given both to variations in the composition of intermediate constituents resulting from solution of the component metals and in other ways, and to the nature of the solid solutions formed when these constituents dissolve in primary solid solutions.

All intermediate constituents have a characteristic space-lattice composed of the two sorts of atoms in certain definite proportions, e.g. CuZn, Cu₅Zn₈. This is the basic composition of the constituent. In some cases the composition cannot vary (e.g. Mg₂Cu), and the characteristic lattice always contains the two kinds of atoms in these proportions. In others, however, the composition can vary within certain limits. This means that the type of lattice remains the same while the relative proportions of the two kinds of atoms alter, and this is accompanied by a change in the lattice dimensions just as in primary solid solutions. In terms of crystal structure the variation in composition is described as a replacement of atoms of metal *X* by atoms of metal *Y*, or of atoms of metal *Y* by atoms of metal *X*. In terms of constitutional diagrams it is described as the solution of *Y* or *X* in the intermediate constituent. The basic composition of CuZn is 50.7 per cent. of zinc and 49.3 per cent. of copper. The range of composition over which this constituent is stable varies with temperature, but at 800° C. it extends from 39 to 55 per cent. of zinc. In the basic crystal structure all the *A* and *B* positions (Fig. 120) are occupied by copper atoms, and all the *C* and *D* positions by zinc atoms. As the zinc content increases, zinc atoms occupy some of the *A* and *B* positions in addition to the *C* and *D* positions, whereas when the zinc content decreases, copper atoms occupy some of the *C* and *D* positions in addition to the *A* and *B* positions. Similar changes can occur in all the intermediate constituents that are capable of changing their composition, but in those in which the atoms are not distributed in an ordered manner in the basic lattice *A*, *B*, *C*, and *D*, positions cannot be distinguished and all that can be said is that the relative proportions of the atoms varies.

Although we are dealing with binary alloy systems, a few comments on more complex alloys may be made here. Copper forms primary solid solutions with nickel in all proportions, and with zinc, tin, aluminium,

and manganese up to certain limits. In view of the fact that each of these metals is individually soluble in solid copper it is to be expected that various combinations of them will also be soluble. This is actually the case and copper-rich solid solutions containing several or all of the metals simultaneously can be prepared. Such solid solutions are formed in some industrial brasses, but scientific studies have in the main been confined to alloys containing two elements in addition to the copper. When any combination of zinc, tin, or aluminium is added to copper, the extent to which each is soluble is less than when the metals are added individually. Thus at 800° C. zinc is soluble in solid copper to the extent of 33.8 atoms per cent. and aluminium to the extent of 18 atoms per cent. When these metals are added simultaneously, the solubility limits at 800° C. are as follows:

Zn 25.3 atoms per cent.	Al 4.63 atoms per cent.
Zn 16.96 atoms per cent.	Al 9.0 atoms per cent.
Zn 9.65 atoms per cent.	Al 13.2 atoms per cent.

Thus the presence of zinc decreases the solubility of aluminium and that of aluminium decreases the solubility of zinc. This is what would be expected, for as the copper lattice can incorporate a given proportion of zinc atoms or aluminium atoms when either kind is present alone, the solubility of each should decrease in the presence of the other. Furthermore, as copper can dissolve more zinc atoms than aluminium atoms, one aluminium atom would be expected to be equivalent to more than one zinc atom. The above figures show this to be the case, for as the atomic percentage of aluminium atoms increases from 0 to 4.63 that of zinc atoms decreases from 33.8 to 25.3, and as the atomic percentage of aluminium atoms increases from 13.2 to 18 that of zinc atoms decreases from 9.65 to 0. Similar changes occur when any two of a large number of metals are added to copper, e.g. Zn, Al, Sn, Cd, Sb, As, &c. When, however, nickel is added to copper along with zinc, it increases the solubility of zinc. The same appears to apply to manganese. Thus, although the atoms of these elements replace copper atoms, and although manganese is only soluble in copper to a limited extent, yet the presence of these elements appears to increase the capacity of the lattice to incorporate zinc atoms. In other words, in primary solid solutions based on copper, nickel and manganese atoms function like copper atoms in so far as the solution of zinc is concerned.

In addition to the variations in composition that can be produced by altering the relative proportions of the two metals forming a primary solid solution further variations can be obtained by adding other metals. This also applies to certain intermediate constituents. Thus CuZn and Cu₅Zn₈, which can vary in composition over a range through an increase or decrease in the zinc content, may also vary in composition by dissolving other elements such as nickel, aluminium, and tin in them. Here nickel functions like copper, and aluminium and tin like zinc. Other intermediate constituents that cannot vary in composition as a result of

changes in the relative proportions of their components cannot dissolve other metals. These constituents may, however, change in composition in one particular way. The iron-carbide Fe_3C is a constituent of fixed composition, and the relative proportions of the two elements cannot vary. Iron atoms may, however, be replaced to a certain extent by chromium atoms while the relative proportions of $\text{Fe} + \text{Cr}$ and carbon remain constant, i.e. $(\text{Fe}, \text{Cr})_3\text{C}$. The limit of this substitution is reached when the carbide contains 15 per cent. of chromium. Carbides of higher chromium content have the formulae Cr_3C_2 , Cr_7C_3 , and Cr_4C in which chromium atoms may be replaced within certain limits by iron atoms.

When one metal dissolves another either in the liquid or the solid state the solute is said to be atomically dispersed, i.e. the solution consists of atoms of the solute dispersed throughout the solvent. Little is known about the constitution of liquid metallic solutions, but in view of the fact that a metal crystal is known to consist of a lattice of free electrons and ions it is clear that the above description is not strictly accurate. Actually in solid solutions as in pure metals the atoms are ionized to some extent and an electron lattice is formed from the free electrons. The expression 'atomically dispersed' is convenient, however, in that it indicates that in a solid solution of one metal in another individual atoms of the solute are distributed throughout the solvent. The same conditions prevail when one metal dissolves two, three, or four others, e.g. when copper dissolves zinc, tin, and aluminium, but the question arises, what happens when a metal dissolves an intermediate constituent?

When a piece of steel that has previously been slowly cooled is heated through a certain range of temperature, crystals of iron-carbide (Fe_3C) are observed to dissolve in solid iron giving rise to a homogeneous solid solution. When the steel is cooled again the crystals of iron-carbide reappear. The simplest description of this reversible change is to say that iron-carbide has been dissolved and redeposited. Similarly, when an aluminium-copper alloy containing 4 per cent. of copper is heated, crystals of CuAl_2 dissolve in aluminium as the temperature rises and above 500°C . a homogeneous solid solution is produced. The crystals reappear when the alloy is cooled. A further example of a slightly different kind is provided by aluminium alloys containing magnesium and silicon. These last two form an intermediate constituent Mg_2Si and in aluminium alloys containing more than 0.27 and less than 1.85 per cent. of this constituent the crystals dissolve during heating and reappear during cooling. In both these examples the simplest way of describing the change is to say that CuAl_2 and Mg_2Si dissolve in aluminium during heating and are redeposited during cooling.

Now while it is true that in the examples quoted above intermediate constituents dissolve during heating and reappear on cooling, it does not necessarily follow that they retain their identity while in solution. There are three possibilities. Firstly, the constituent may decompose on going

into solution. In the case of iron-carbide this would mean that carbon would diffuse out of the carbide into the iron and the iron atoms associated with carbon in the carbide would take up normal positions on the iron lattice. Secondly, the constituent may retain its identity in solid solution by dissolving as molecules, e.g. Fe_3C , CuAl_2 , or Mg_2Si . In the case of iron-carbide this would mean that groups consisting of three iron atoms and one carbon atom diffuse into the iron on heating and diffuse out again on cooling. Finally, the constituent may retain its identity in solid solution in some other way. If such conditions arose, magnesium and silicon dissolved as Mg_2Si would differ from magnesium and silicon dissolved separately, and iron atoms belonging to carbide would differ from the other iron atoms among which they were dissolved.

At the present time there is little direct evidence as to the condition of intermediate constituents in solid solution, but a number of arguments have been put forward in support of one view or another. The prevailing opinion is that these constituents lose their identity when they go into solid solution, i.e. that the first possibility is the correct one. The principal argument in support of this is the difficulty of accounting for the diffusion of groups of atoms such as Fe_3C , CuAl_2 , and Mg_2Si through solid crystals. This argument does not dispose of the possibility of the constituents retaining their identity in some other way, but as no clear description of what this involves has yet been given it is usual to neglect this possibility. As will be explained in the next chapter, even small molecules like those of hydrogen cannot diffuse in solid metals, and gases generally cannot diffuse until they have been converted to the atomic state. In view of this it is not to be expected that molecules of intermediate constituents will diffuse into and out of solid metals. If one of the constituents of the intermediate phase is also the basis metal of the alloy (e.g. Fe_3C in steel), solution and deposition need not involve any movement of the iron atoms. When this constituent dissolves, the carbon simply diffuses into the surrounding iron and the iron atoms in the carbide take up normal positions on the iron lattice. When it is redeposited, the carbon atoms form the Fe_3C lattice with the iron atoms already situated at the point of precipitation. When, however, neither of the components of the intermediate phase is the basis metal of the alloy (e.g. Mg_2Si in aluminium), different conditions are realized. When this compound dissolves in aluminium, both magnesium and silicon diffuse into the basis metal. When it is deposited, both diffuse out again, and if they do not diffuse at the same rate the formation of the compound will depend on the slowest rate of diffusion. At low temperatures diffusion is slow, and if the rate of diffusion of the two elements is very different there will be a tendency for a compound of different composition to form. This has been shown to occur in the case of Mg_2Si in aluminium. In steels of high chromium content, chromium carbide is formed instead of iron carbide, and it is explained in Chapter XII that under certain conditions this carbide may be precipitated from

solution in iron in such a way that it is formed by carbon diffusion from all over the iron crystals and chromium drawn from the vicinity of the boundaries. This further suggests that the compound does not exist as such in solution, and in what follows intermediate constituents will be considered to have a definite and independent existence only when they occur as crystals with the appropriate structure. In solid solutions which result from their dissolution in a pure metal or a primary solid solution the component elements of intermediate constituents will be considered to exist independently. At the same time, however, expressions such as 'on heating through the range X to $Y^{\circ}\text{C}$. Fe_3C dissolves in iron' or 'during slow cooling CuAl_2 is deposited from solution' will be used to describe what occurs without meaning that these constituents exist as such in solution.

BINARY ALLOY SYSTEMS IN WHICH INTERMEDIATE CONSTITUENTS ARE FORMED

In several well-known alloy systems as many as four or five intermediate constituents are formed, and when the two terminal constituents (i.e. the pure metals or primary solid solutions based on them) are added, the number of phases in the system becomes six and in some cases more. Each of these phases is stable over a certain range of composition and these ranges are separated by regions in which two phases occur. Furthermore, the relations between the phases alter with temperature, and frequently phases which exist at elevated temperature disappear at lower temperature and vice versa. Thus binary alloy systems in which intermediate constituents are formed may be very complicated and their full consideration would occupy a large amount of space. As it is impossible to undertake such a full description here it is necessary to consider how the subject may be treated without omitting anything essential.

In the first place it may be said that the same general considerations apply to all systems, and in this respect one system containing intermediate constituents does not differ from another, nor do systems of this kind differ from those in which no intermediate constituents are formed. Furthermore, those alloy systems in which intermediate constituents are formed are not of practical importance over their whole range of composition. Some systems of the types already dealt with are of practical importance over the whole range, e.g. the copper-nickel and iron-nickel alloys, and as these are comparatively simple they are always considered as a whole. The systems containing intermediate constituents are, however, only of practical importance at one or both ends, and because of this the ends of the systems have been studied more intensively than the remainder. In dealing with these systems attention will therefore be given in the first place to their general characteristics, and then two types of systems that cover the useful ranges of composition of industrially important alloys will be considered. The various systems belonging to each of these types are described in detail in Parts V and VI.

As a general example of a system in which intermediate constituents are formed the magnesium-copper alloys may be considered. The diagram for this system is shown in Fig. 122. Two intermediate constituents are formed, namely MgCu_2 which contains 83.94 per cent. of copper by weight and melts at 819°C ., and Mg_2Cu which contains 56.65 per cent. of copper by weight and melts at 568°C . At 722° 1. per cent. copper can dissolve in solid solution as indicated by point *b*; but the solubility of copper in magnesium is negligible, being only 0.03 per

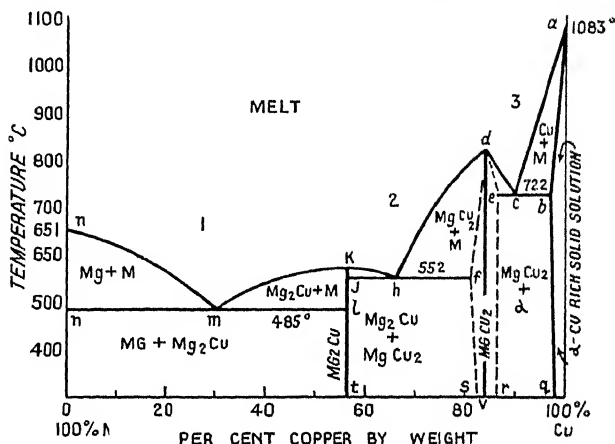


FIG. 122. The Cu-Mg system.

cent. at 485°C . MgCu_2 is capable of dissolving between 2 and 3 per cent. of either of its components, i.e. it can vary in composition over a range by the substitution of magnesium for copper atoms or of copper for magnesium atoms in the basic MgCu_2 lattice. Mg_2Cu is incapable of varying in this way. Copper has a face-centred cubic lattice and magnesium a close-packed hexagonal lattice. MgCu_2 has a complex cubic lattice with 24 atoms per unit cell, i.e. 8 Mg and 16 Cu. The length of the side of the cell is $7.021\text{--}7.036\text{ \AA}$. Mg_2Cu has a complex rhombic lattice with 48 atoms per unit cell, i.e. 32 Mg and 16 Cu.

The complete diagram shown in Fig. 122 can be regarded as consisting of three portions separated by the lines *dv* and *kt* and denoted by the numbers 1, 2, and 3. Portion 1 is a system of Type 1 in which Mg and Mg_2Cu are involved. Portions 2 and 3 are systems of Type 3 in which Mg_2Cu and MgCu_2 , and MgCu_2 and Cu are respectively involved. The complete liquidus curve *nmkhdca* consists of six branches *nm*, *mk*, *kh*, *hd*, *dc*, and *ca*. Twelve different kinds of alloys may be distinguished according to their constitution on solidification. These are as follows:

Composition	Constitution
1. 100–97.4% Cu (<i>b</i>)	α Primary Solid Solution based on Cu.
2. 97.4–90% Cu (<i>b-c</i>)	Skeleton Crystals of α in matrix of eutectic of α and MgCu_2 .

<i>Composition</i>	<i>Constitution</i>
3. 90% Cu (<i>c</i>)	Eutectic of α and MgCu_2 .
4. 90-86.5% Cu (<i>c-e</i>)	Crystals of MgCu_2 in matrix of eutectic of α and MgCu_2 .
5. 86.5-81% Cu (<i>e-f</i>)	MgCu_2 . Pure or dissolving either Cu or Mg.
6. 81-65.5% Cu (<i>f-h</i>)	Crystals of MgCu_2 in matrix of eutectic of MgCu_2 and Mg_2Cu .
7. 65.5% Cu (<i>h</i>)	Eutectic of MgCu_2 and Mg_2Cu .
8. 65.5-56.65% Cu (<i>h-j</i>)	Crystals of Mg_2Cu in matrix of eutectic of MgCu_2 and Mg_2Cu .
9. 56.65% Cu (<i>j</i>)	Mg_2Cu .
10. 56.65-30% Cu	Crystals of Mg_2Cu in matrix of eutectic of Mg_2Cu and Mg.
11. 30% Cu (<i>m</i>)	Eutectic of Mg_2Cu and Mg.
12. 30-0.03% Cu (<i>m-n</i>)	Crystals of Mg in matrix of eutectic of Mg_2Cu and Mg.

The structure of eutectics is considered in a later section of this chapter, but it has already been explained that the simultaneous formation of the two constituents at a eutectic point usually results in an intimate structural relationship between them. Some structures formed in the alloys under discussion may, therefore, be described and illustrated by micrographs taken by Jones (78) whose work has contributed largely to the determination of the copper-magnesium diagram. Fig. 123 shows the Mg- Mg_2Cu eutectic in an alloy of composition *m* (Fig. 122). The two constituents combine to give a eutectic structure with a definite pattern. Fig. 124 represents an alloy containing 46.5 per cent. Cu and is characteristic of alloys that lie between *m* and *l*. The long white crystals are Mg_2Cu and the matrix is the eutectic shown in Fig. 123. Fig. 125 shows the structure of an alloy of composition *h*, i.e. the Mg_2Cu - MgCu_2 eutectic. Its structure is quite different from that shown in Fig. 123 but again the two constituents form a pattern. Fig. 126 shows the structure of an alloy containing 71.3 per cent. of copper. This alloy lies just to the right of *h* and the white crystals are MgCu_2 while the matrix is the eutectic shown in Fig. 125. Finally, Fig. 127 represents an alloy containing 92.15 per cent. Cu (i.e. just to the right of *c*) and shows crystals of α primary solid solution in a matrix of eutectic *c* (i.e. α - MgCu_2). This last closely resembles the Mg- Mg_2Cu eutectic shown in Fig. 123, while both differ from the Mg_2Cu - MgCu_2 eutectic shown in Fig. 125. It will be observed that the crystals of α in Fig. 127 and of MgCu_2 in Fig. 126 are skeleton crystals of the type illustrated in Fig. 98 and typical of pure metals and primary solid solutions, whereas the crystals of Mg_2Cu shown in Fig. 124 are of quite a different character. The difference between the crystals of MgCu_2 and Mg_2Cu respectively is of general significance in relation to intermediate constituents, for whereas some of them form crystals which develop in the first place as skeletons, others form crystals of a more or less regular shape that grow as compact masses.



FIG. 123. $\text{Mg-Mg}_2\text{Cu}$ eutectic. $\times 250$.
(*Journal of the Institute of Metals.*)



FIG. 124. Mg_2Cu in eutectic matrix. $\times 50$. (*Journal of the Institute of Metals.*)



FIG. 125. $\text{Mg}_2\text{Cu-MgCu}_2$ eutectic. $\times 250$.
(*Journal of the Institute of Metals.*)



FIG. 126. MgCu_2 in eutectic matrix. $\times 250$.
(*Journal of the Institute of Metals.*)

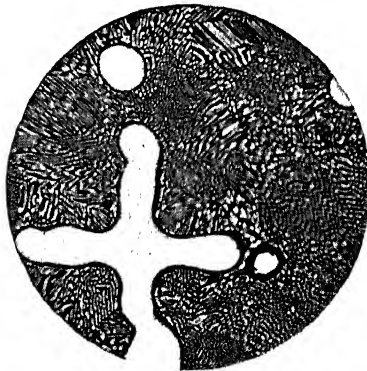
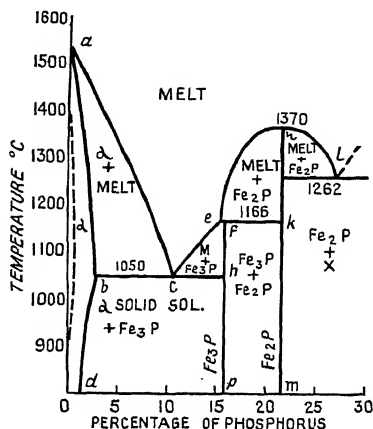


FIG. 127. Cu in eutectic matrix. $\times 250$.
(*Journal of the Institute of Metals.*)

As a further example of a system in which intermediate constituents are formed the iron-phosphorus alloys may be described. Fig. 128 shows the constitutional diagram up to 30 per cent. phosphorus as determined by Haughton (79). Two intermediate constituents are formed, namely, Fe_3P and Fe_2P which contain 15.6 and 21.5 per cent. of phosphorus respectively and are represented in the diagram by the lines phf and mkn . At $1,050^\circ\text{C}$. iron can dissolve 2.8 per cent. of phosphorus as indicated by point b and this solid solution is known as α . Neither Fe_3P nor Fe_2P is capable of dissolving appreciable amounts of either of the components. Within the loop formed by the dotted line at the left of the diagram iron has a face-centred cubic lattice (i.e. it is γ -iron). The meaning of this loop (which occurs in many alloy systems based on iron) is considered in Chapter VI. In so far as the remainder of the diagram is concerned it is body-centred cubic α -iron that is involved. Fe_3P has a body-centred tetragonal lattice and Fe_2P a hexagonal lattice.



128. The iron-phosphorus alloys.

The principal difference between the iron-phosphorus and the copper-magnesium systems is that the two intermediate constituents are connected by a peritectic in the former and a eutectic in the latter. efk (Fig. 128) is the peritectic horizontal. In alloys that lie between f and k solidification begins with the formation of Fe_2P (represented by the line nkm), and as the temperature falls this constituent continues to form while the liquid changes in composition along ne . When the liquid reaches e Fe_3P begins to form. This continues at constant temperature until solidification is complete and thus all alloys between f and k consist of a mixture of Fe_3P and Fe_2P . In alloys that lie between e and f solidification again begins with the formation of Fe_2P , and when the liquid reaches e there is a reaction between the melt and Fe_2P which results in the transformation of the latter into Fe_3P . Solidification then continues as the temperature falls and more Fe_3P is formed direct from the liquid. Ultimately the melt reaches the eutectic point C and solidification is completed by the formation of the eutectic of α (composition b) and Fe_3P . Apart from the peritectic change the general features of the iron-phosphorus and the copper-magnesium diagrams are the same. Within the range of composition up to 27 per cent. P (point l) nine types of alloys may be distinguished. These are as follows:

Composition	Constitution
1. 0-2.8% P (b)	α primary solid solution based on iron.
2. 2.8-10.5% P ($b-c$)	Crystals of α in matrix of eutectic of α and Fe_3P .

Composition	Constitution
3. 10.5% P (<i>c</i>)	Eutectic of α and Fe_3P .
4. 10.5–15.6% P (<i>c-h</i>)	Crystals of Fe_3P in matrix of eutectic of α and Fe_3P .
5. 15.6% P (<i>h</i>)	Fe_3P .
6. 15.6–21.5% P (<i>f-k</i>)	$\text{Fe}_3\text{P} + \text{Fe}_2\text{P}$.
7. 21.5% P (<i>k</i>)	Fe_2P .
8. 21.5–27% P (<i>k-l</i>)	Crystals of Fe_2P in matrix of eutectic of Fe_2P and X.
9. 27.0%	Eutectic of Fe_3P and X.

As a final illustration of the general features of systems containing intermediate constituents a portion of the copper-zinc system may be described. The appropriate portion of the diagram is shown in Fig. 129.

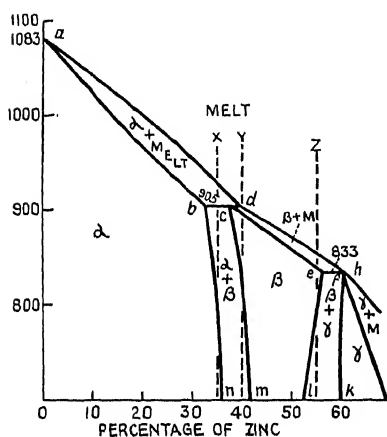


FIG. 129. The copper-zinc alloys.

Within the range of composition shown two intermediate constituents are formed, viz. CuZn (β) and Cu_5Zn_8 (γ). When the primary solid solution of zinc in copper (α) is added there are three constituents. α has the face-centred lattice characteristic of copper, β has a body-centred cubic lattice, and γ the complex cubic lattice already described. Each constituent is capable of varying in composition over a considerable range and the different constituents are connected by peritectic transformations as a result of which two constituents are formed in certain alloys at solidification. Within the range of composition shown in Fig. 129 five different types of alloys may be distinguished according to their constitution at solidification. These are as follows:

1. Alloys that lie to the left of *b* solidify as the primary solid solution α .
2. Alloys that lie between *b* and *c* solidify as mixtures of α of composition *b* and β of composition *c*.
3. Alloys that lie between *c* and *e* solidify as β , i.e. solutions of copper or zinc in CuZn . (Those between *c* and *d* begin to solidify as α but this changes to β at the peritectic temperature 905°C .)
4. Alloys that lie between *e* and *f* solidify as β of composition *e* and γ of composition *f*.
5. Alloys that lie to the right of *f* solidify as γ , i.e. solutions of copper or zinc in Cu_5Zn_8 .

This system is fully considered in Chapter XV.

Alloy Systems, Types 4 and 5.

It now remains to describe two types of alloy systems that cover the useful ranges of composition of industrially important alloys. In systems of Type 4 the added element is soluble in the basis metal to a limited extent and when this is exceeded a eutectic of the primary solid solution and an intermediate constituent appears. In other words, the portion of the system that relates to industrially important alloys is similar to the right hand end of the copper-magnesium system (Fig. 122) or the left hand end of the iron-phosphorus system (Fig. 128). Two very important series of industrial alloys give systems of this kind, namely, the iron-carbon and the aluminium-copper alloys. At the temperature of solidification carbon is soluble in solid iron to the extent of 1.7 per cent. Alloys containing less than this amount solidify as solid solutions. Alloys containing more than this solidify as crystals of the primary solid solution in a matrix of a eutectic of this solid solution and Fe_3C . Similarly, at the temperature of solidification copper is soluble in solid aluminium to the extent of 5.65 per cent. Alloys containing less than this solidify as solid solutions, alloys containing more solidify as solid solution crystals plus a eutectic of the solid solution and CuAl_2 .

In systems of Type 5 the added element is soluble in the basis metal to a limited extent, and when this is exceeded alloys consisting of two constituents formed at a peritectic are produced. When the proportion of the added element is further increased the alloys consist entirely of the second constituent, and a still further increase gives rise to alloys consisting of a mixture of this second and a third constituent. In other words the portion of the system that relates to industrially important alloys is similar to the copper-zinc system represented in Fig. 129. In some alloys of this type the useful range is within the limits of the primary solid solution (α), in others it extends through the first range of mixed phases ($\alpha+\beta$) to the range in which the second constituent is formed (β), and in a few cases it extends into the second range of mixed phases ($\beta+\gamma$). It must be borne in mind, however, that at atmospheric temperature the ranges of composition within which constituents exist differ from those within which they exist at solidification. This aspect of the subject is dealt with in the next chapter.

Five types of alloy systems that relate to industrially important alloys have now been described, and in Table 24, forty-seven binary alloy systems are classified according to these types. The sixth type is that in which the component metals are immiscible or only partly miscible when molten.

TABLE 24

Binary Systems relating to Industrially Important Alloys classified according to Types described in Chapter V

The systems are classified according to the constitutional relations in the range of solidification. In Types 1, 2, 3, and 6 the classification applies to the

systems as a whole. In Types 4 and 5 it applies to the useful range at one end of the system.

Type 1

The two metals are almost completely insoluble in each other when solid.
Zn-Sn. Cu-Bi.

Type 2

The two metals are soluble in each other in all proportions when solid.
Fe-Cr. Fe-V. Cu-Ni. Ni-Co.

Type 3

(A) Each metal is soluble in the other to a limited extent when solid and alloys solidifying as two phases have a eutectic.

Cu-Ag. Pb-Sb. Pb-Bi. Pb-Cd. Pb-Sn. Ni-Cr. Sn-Bi. Sn-Cd.

(B) The alloys are similar to the above but there is solid solubility at one end only.

Al-Si.

(C) The systems are intermediate between Type 2 and Type 3. Owing to the two modifications of iron there is a peritectic connecting solid solutions in α -Fe with those in γ -Fe. These latter solid solutions form a continuous series with a solid solution based on the other metal.

Fe-Co. Fe-Ni.

(D) The alloys are similar to the above but the solid solution in γ -Fe does not form a continuous series with that based on the other metal.

Fe-Mn. Fe-Cu.

Type 4

At the useful end the added metal is soluble in the basis metal (given first) to a limited extent. When this limit is exceeded, a eutectic of the primary solid solution and an intermediate constituent appears.

Al-Cu. Al-Fe. Al-Mg. Al-Mn. Al-Mg₂Si. Al-Ni. Cu-P. Cu-O. Cu-As. Cu-Sb. Cu-Ti. Fe-C. Fe-Mo. Fe-Si. Fe-W. Mg-Al. Mg-Zn. Ni-Al. Zn-Al.

A primary solid solution (basis metal given first) is followed by a two-phase region, then by an intermediate constituent, then by another two-phase region and another intermediate constituent.

(A) The useful range is confined to that of the primary solid solution.

Cu-Si. Cu-Cd. Cu-Be. Fe-Al. Pb-Ca.

(B) The useful range extends beyond that of the primary solid solution.

Cu-Al. Cu-Sn. Cu-Zn. Sn-Sb.

Type 6

Two liquids are formed.

Cu-Pb. Pb-Zn. Al-Pb. Cu-Co.

Alloy Systems, Type 6. The Two Metals are not Completely Miscible in the Liquid State.

There are three varieties of this type of system: (A) the two metals are completely immiscible in the liquid and solid states, (B) the two metals

are partly miscible in the liquid state and immiscible in the solid state, and (C) the two metals are partly miscible in both the liquid and solid states. The aluminium-lead alloys are an example of (A), the copper-lead alloys of (B), and impure copper-iron alloys of (C). Case B may be described in detail and the others as modifications of this.

The constitutional diagram for copper-lead alloys is shown in Fig. 130. The line cd represents the solubility of lead in molten copper and line hfe the solubility of copper in molten lead. As these two lines approach each other with rising temperature it means that the solubility of each metal in the other is increasing. At a sufficiently high temperature the two lines should meet and above this the two metals would be completely miscible. The temperature at which this occurs has not been determined but it is considered to be well above $1,500^{\circ}\text{C}$. If

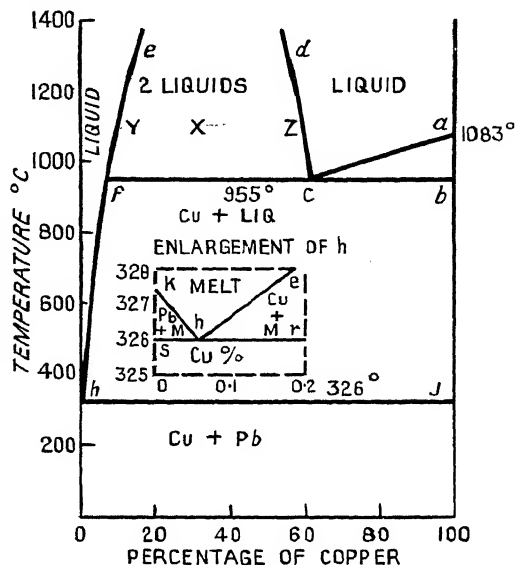


Fig. 130. Cu-Pb alloys.

the temperature and composition of a liquid alloy can be represented by a point lying on the right of cd , the alloy is a homogeneous liquid solution of lead in copper. If it can be represented by a point to the left of hfe , the alloy is a homogeneous liquid solution of copper in lead, and if it can be represented by a point between fe and cd , it consists of two liquids the compositions of which are represented by the appropriate points on fe and cd . Thus the alloy X at $1,100^{\circ}\text{C}$. consists of a mixture of liquids of composition Y and Z respectively and the relative proportions of these are such that

$$\frac{\text{amount of Y}}{\text{amount of Z}} = \frac{ZX}{YX}.$$

If the temperature and composition of an alloy can be represented by a point in the area $hfcbj$, it consists of solid copper and liquid of the composition indicated by the appropriate point on hf . h is really a eutectic point, but as it occurs at 0.06 per cent. of copper and 326°C . it cannot be distinguished in the diagram from the melting-point of lead. In the inset, however, the conditions at h are shown, and it will be seen that there is a small area lhs in which alloys consist of solid lead plus liquid. Below hj all alloys are solid and consist of mixtures of copper and lead.

In a system of this kind four kinds of alloys may be distinguished. If the composition lies to the right of c (62 per cent. Cu), solidification begins on the line ac and copper crystals begin to grow. This continues as the temperature falls and the liquid moves along ac to c . Then the formation of solid copper continues at constant temperature while the liquid changes in composition along cf . This is known as a 'monotectic' reaction. After the liquid attains the composition f (7.5 per cent. Cu), solidification continues as the temperature falls. The copper crystals continue to grow and the liquid moves along the line fh to h . At h solidification is completed by the formation of a eutectic of copper and lead. If the composition of an alloy lies between f and c (7.5-62 per cent. Cu), it consists of two liquids when solidification begins. The liquid of composition c begins to solidify at 955°C . and solid copper is formed. This continues at constant temperature until this liquid reaches composition f . All the liquid is now of composition f and as the temperature falls solidification continues as described above. If the composition of an alloy lies between h and f , solidification begins on the line hf and continues as the temperature falls to the eutectic. If the composition lies to the left of h , solidification begins on the line kh (inset). Pure lead is formed as the temperature falls and solidification is completed at the eutectic.

In the case of two metals that are completely immiscible in the liquid state all alloys are similar. If A has a higher freezing-point than B , solidification begins at the freezing-point of A . All the A solidifies at constant temperature and no further change takes place until the freezing-point of B is reached, when all the B solidifies at constant temperature. In the case of two metals that are partially miscible in both the liquid and the solid state solutions are produced instead of pure metals as described above. An example of this is provided by the alloys of copper and iron when some impurities are present. This system is considered in Chapter XII and the diagram is shown on page 957. This diagram is based on the most recent investigations and relates to pure alloys which exhibit complete miscibility. In earlier investigations, however, as a result of the presence of small amounts of carbon, a gap in miscibility was found to exist between 24 and 85 per cent. of copper, the remainder of the diagram being essentially as shown on page 957. As thus determined the system was an example of the conditions realized when the two metals are partially miscible in both the liquid and solid states. Thus, at the temperature of the liquidus, copper was soluble in molten iron to the extent of 24 per cent. and in solid iron to the extent of 7.5 per cent. as indicated by point I , Fig. 418. At the other end iron was soluble in liquid copper to the extent of 15 per cent. and in solid copper to the extent of 4 per cent. as indicated by point M .

When two liquids exist in a molten alloy they tend to separate into two layers with the heavier metal at the bottom. Agitation of the molten alloy will prevent this and by such means one liquid can be retained in the

form of globules distributed throughout the other. Alloys that consist of two liquids when molten are rarely made, and when partially miscible metals are alloyed the range of composition used is within the limits of liquid solubility of one metal in the other. The best-known alloys of this kind are those made by adding up to 30 per cent. of lead to copper. In such alloys the copper solidifies first and freezing is completed by the formation of a eutectic which is practically pure lead. Most of the copper solidifies above or at the monotectic temperature ($955^{\circ}\text{C}.$), and during cooling to $326^{\circ}\text{C}.$ an opportunity is provided for the copper crystals to float upwards and the lead to drain downwards. The results actually obtained depend on the relative proportions of copper and lead and the rate of cooling. If the proportion of copper is such that the alloy consists at the conclusion of the monotectic reaction of skeleton crystals that almost fill space, the remaining liquid will have difficulty in draining away through the small interstices of the skeletons. Consequently, the solid alloy will consist of copper crystals with small globules of lead in the interstices of the skeletons. As the amount of copper decreases, the volume of solid existing at the end of the monotectic reaction also decreases, and more opportunity is allowed for the liquid and solid to segregate during cooling to $326^{\circ}\text{C}.$ The amount of segregation that occurs depends on the time taken to cool through this range. In practice a uniform distribution of lead is obtained in alloys containing up to 15 per cent. of this metal when these are cooled at a moderate rate. A fairly uniform distribution can be secured in alloys containing up to 30 per cent. of lead by chill casting, i.e. by casting in a metal instead of a sand mould.

EUTECTICS

Eutectics occur in many binary alloy systems and their principal characteristic is that they are formed by the simultaneous crystallization of two constituents. In systems of the zinc-tin type (Fig. 107) both constituents are pure metals, in those of the copper-silver type (Fig. 117) both are primary solid solutions, while in those of the aluminium-silicon type one constituent is a primary solid solution and the other a pure metal. In all systems of Type 4 (Table 24) the eutectic consists of a primary solid solution and an intermediate constituent, but in other systems (e.g. the copper-magnesium, Fig. 122) eutectics consisting of two intermediate constituents are formed and in others (e.g. copper-oxygen) the eutectic is between a substantially pure metal and an intermediate constituent.

Owing to their simultaneous crystallization from the melt the two constituents of a eutectic are frequently arranged in a definite pattern as shown in Figs. 123, 125, and 127. In this way various different kinds of structures are formed, but there are many cases in which the simultaneous crystallization of two constituents does not lead to the production of a definite eutectic structure. Besides variations in the characteristics of

the eutectics formed in different systems, the eutectic in any given system may be affected by several factors. In all cases an increase in the rate of cooling produces an increase in the fineness of the eutectic, and in certain alloys (e.g. those of aluminium and silicon) it produces a complete change in the character of the eutectic. Sometimes the character of the eutectic varies according to which of the constituents is present in excess of the eutectic proportion, and when only a small amount of liquid is present when the eutectic reaction occurs, the structural aspects of the change are different from those that arise when larger quantities are present. It must be remembered that eutectic structures are three-dimensional patterns while microscopic examination is carried out on plane sections. Similar three-dimensional patterns may give rise to quite different two-dimensional patterns when cut in different ways by the plane examined, and consequently it is sometimes difficult to distinguish variations arising from differences in the structure from those arising from differences in the way in which a given structure is transversed by the plane examined.

Eutectic structures are in general characterized by their fineness, but this term has a relative rather than an absolute meaning. In any particular specimen containing primary crystals and eutectic the constituents in the eutectic are small compared with the primary crystals (see Figs. 124, 126, and 127). But the size of the constituents in the eutectic, like that of the primary crystals, is controlled by the rate of cooling through the range of solidification, and the structure of a very slowly cooled eutectic may be coarser than that of the primary crystals in a rapidly cooled alloy.

In general, the constitution of an alloy is determined by the nature of the constituents and the relative amounts in which they are present, while the structure is determined by the size and shape of the particles of the constituents and their arrangement with respect to each other. Accordingly, a eutectic is a structural feature rather than a constituent, and in Fig. 117 all solid alloys are represented as consisting of a mixture of a solid solution of copper in silver and one of silver in copper. This practice is adhered to in Figs. 122 and 128. There is some justification, however, for regarding a eutectic as a constituent, for the intimate arrangement of the two constituents gives it properties that are different from those of other mixtures of the same constituents. It is really more accurate to describe the alloys that lie to the left of *E* (Fig. 117) as consisting of primary crystals of silver-rich solid solution and eutectic rather than as consisting of a mixture of the two solid solutions. Both descriptions will be considered as constituents. Another type of constituent which resembles a eutectic and is known as a eutectoid is described in the next chapter. Four general types of alloy constituents may thus be distinguished: (1) pure metals, (2) primary solid solutions, (3) intermediate constituents, and (4) eutectics and eutectoids. Constituents of

the last type consist, of course, of mixtures of two (or three) constituents of the other types.

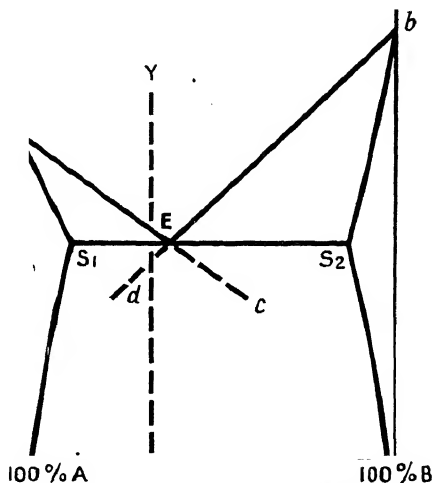
Before dealing briefly with eutectic structures it is necessary to give further attention to eutectic systems. The general type of diagram for such a system may be represented by Fig. 131. Both A and B may be pure metals (e.g. copper and silver, Fig. 117) or intermediate constituents (e.g. Mg_2Cu and MgCu_2 , Fig. 122) or one may be a pure metal and the other an intermediate constituent (e.g. iron and Fe_3

128). The limits of solid solubility of each constituent in the other represented by S_1 and S_2 may be negligible as in the zinc-tin system (Fig. 108), considerable as in the nickel-chromium system (Fig. 118), or different at each end as in the iron- Fe_3P system (Fig. 128). The eutectic point E may in general be situated at any point between 100 per cent. A and 100 per cent. B (see Figs. 107, 117, 118, 122, 128, and 130).

Under equilibrium conditions any alloy in the system AB (Fig. 131) begins to solidify when

cooled to the appropriate point on aEb . If the composition of the alloy lies to the left of E , solidification begins when it is cooled to the line aE ; if to the right of E , it begins when it is cooled to the line bE . In the first case A , and in the second case B , is deposited. In both cases solidification proceeds as the temperature falls and the composition of the liquid alters along the line aE or bE . Now the real meaning of the lines aE and bE is that liquid cannot persist below them. Thus if liquid of a composition to the left of E is cooled below aE , solid A will tend to form until the liquid attains a temperature and composition represented by a point on aE . The same applies to liquid of a composition to the right of E except that solid B is formed. Point E owes its significance to the fact that it lies on both lines, and if liquid of composition E is cooled below the temperature of E both lines are crossed and crystals of A and B may form simultaneously.

We have seen that, as a result of undercooling, solidification does not begin whenever an alloy is cooled to the temperature represented by the diagram. If the rate of cooling is slow, however, the heat liberated on freezing will raise the temperature to the appropriate level and thereafter solidification will proceed according to the diagram. What we have now to consider is what happens when the rate of cooling is such that



131. General eutectic diagram.

solidification does not proceed according to the diagram. An alloy of eutectic composition may be considered first. If such an alloy is cooled rapidly, solidification will not begin at E nor will the temperature rise to E as a result of the evolution of heat. Thus the eutectic reaction will take place at a temperature below E and this temperature will rise, remain constant, or fall according to the relations between the rates of abstraction and liberation of heat. The effect of this is that the eutectic structure is finer, and in general the fineness of such a structure increases with the rate of cooling. If now we consider an alloy lying just to the right or the left of the eutectic point, e.g. alloy Y (Fig. 131), then under equilibrium conditions it should begin to freeze when cooled to the line aE , but during rapid cooling liquid may be retained unchanged at a temperature below Ed . When the alloy is cooled below Ed it is below aE and bE produced, and under these conditions both the constituents may crystallize at the same time. Thus, if the temperature is prevented from rising above Ed during solidification the alloy Y will solidify as eutectic, and its final structure will be similar to that of an alloy of eutectic composition. The same result may be obtained with an alloy that lies just to the right of E , and consequently there is a range of composition on each side of E within which alloys can be made to solidify completely as eutectic by increasing the rate of cooling. The width of this range increases with the rate of cooling, and in general any alloy will solidify completely as eutectic if it can be cooled into the area dEc before solidification begins.

In several systems the two constituents are unequally affected by the rate of cooling; e.g. in the aluminium-silicon system it is easier to suppress the crystallization of silicon than that of aluminium. If B (Fig. 131) represents aluminium and A silicon, the alloy Y should solidify with the crystallization of silicon followed by the formation of eutectic. Rapid cooling, however, prevents the deposition of silicon as the alloy cools from aE to Ed , and below this theoretically both constituents can freeze. Even then, however, silicon does not crystallize and aluminium skeleton crystals begin to form just as if the alloy was on the aluminium side of the eutectic. When this has proceeded to a certain extent the simultaneous crystallization of both constituents sets in and solidification is thus completed. Thus, by means of accelerated cooling, it is possible to obtain in alloys lying on the silicon side of the eutectic, structures similar to those obtained in alloys lying on the aluminium side. Under equilibrium conditions the eutectic is at 11.6 per cent. silicon, but with rapid cooling primary aluminium crystals can be obtained in alloys containing up to 14 per cent. of silicon. Thus, by increasing the rate of cooling, the eutectic point can be displaced from 11.6 to 14 per cent. and lowered from 577° to 564° C. The addition of about 0.1 per cent. of sodium just before casting has the same effect as rapid cooling, and commercial aluminium-silicon alloys are classified as 'normal' when no sodium has been added and 'modified' when sufficient sodium has been added to produce the effect described above.

It is evident from the foregoing that when both constituents of a
ic are similarly affected by the rate of cooling, alloys on both sides
tic point may be caused to solidify completely as eutectic by
hastening the cooling. When, however, one constituent is affected more
 than the other by such an increase, the eutectic point is displaced towards
 a higher proportion of that constituent. The former conditions are
realized when both constituents are of a similar nature, i.e. when both
are pure metals, primary solid solutions, or intermediate constituents.
The latter conditions result when there is a pronounced difference between
the two constituents, i.e. when one is a pure metal or primary solid solu-
tion and the other a non-metal or an intermediate constituent in which
metallic properties are not pronounced. Silicon, e.g., is a non-metal, and
 similar results to those obtained in aluminium-silicon alloys may also
 be produced in those iron-carbon alloys in which carbon appears as
 graphite. In this case, also, modification may be effected by accelerated
 cooling or by the use of certain additions, as explained in Chapter XIV.

When no primary crystals are formed before the eutectic freezing
 begins, the solidification starts from nuclei scattered throughout the
 melt just as in the freezing of other constituents. From each nucleus a
 unit of structure usually described as a 'eutectic colony' or 'eutectic
 grain' is produced, and solidification is completed when the grains grow-
 ing from different nuclei come into contact. If, however, primary
 crystals are present when the eutectic begins to freeze, it may either
 crystallize as above without regard to the existence of the primary
 skeletons or its formation may begin at the surface of the skeletons and
 proceed from there. In either case the solidification of the eutectic
 continues until the interstices of the skeletons and the spaces between
 them are filled with solid eutectic instead of liquid. The final structure
 normally consists of primary skeletons in a matrix of eutectic, but under
 certain conditions this result is not obtained. If the composition of the
alloy is far removed from the eutectic point, the eutectic change begins
when there is only a small amount of eutectic liquid existing as thin films
in the interstices of the skeletons and the spaces between them. If the
primary crystals are of the constituent A, there is a tendency for the A
in the eutectic liquid to deposit on the existing primary crystals, leaving
B in the interstices. Thus, when the constitutional diagram

indicates that a particular alloy should consist mainly of primary crystals
 with only a small amount of eutectic (e.g. as shown in Fig. 100), it is
 usual to find that a eutectic structure is not produced at all, and the
 final structure consists of primary crystals of the predominant metal
 with films or globules of the other in their interstices. Such conditions
 tend to result in all alloys that are situated near the ends of eutectic
 systems, and they may also be realized in alloys that are not situated
 near the end of a system when the eutectic point is itself near one end
 of the system. Thus, in the copper-lead system (Fig. 130), the eutectic
 occurs at 0.06 per cent. of copper and in all alloys containing appreciably

more than this amount the small quantity of copper in the eutectic deposits on the existing copper crystals, leaving pure lead in the spaces between them. Similar results are obtained in the copper-bismuth and iron-iron sulphide systems.

Another respect in which the formation of a eutectic frequently departs from the normal is when it takes place in such a way that the primary crystals of A are separated from the eutectic by a film of B . This is explained as follows: When the residual liquid in alloy Y (Fig. 131) reaches the eutectic point E , primary crystals of A are already in existence and no other nuclei are required for the crystallization of this constituent in the eutectic. Before B can crystallize, however, suitable nuclei must appear, and this process tends to be delayed by under-cooling. Thus B may not crystallize as soon as the liquid reaches E , and the crystallization of A will continue while the liquid changes in composition along Ec . When B does begin to deposit it will tend to do so rapidly so as to bring the liquid back to E . Thus, films of B are deposited on the primary crystals of A , and when the liquid is restored to the equilibrium composition the simultaneous crystallization of the two constituents can begin. The conditions that lead to the formation of a film of B between the eutectic and the primary crystals of A are very similar to those that give rise to structures in which films of B take the place of eutectic. The principal difference is that in the latter case the formation of the films of B results in exhaustion of the liquid, while in the former some liquid still remains to undergo the true eutectic change. Furthermore, whereas the latter conditions are realized in alloys that lie near the ends of systems, or in systems in which the eutectic point is near one end, the former may be realized in nearly all other alloys.

In describing the alloys of copper and silver it was explained that when the rate of cooling is too fast to permit equilibrium to be maintained, eutectic appears in alloys that lie within the limits of solid solubility, i.e. lie to the left of S_1 or the right of S_2 (Fig. 131). If the cooling is just slightly accelerated this can only occur in alloys that lie close to S_1 or S_2 , but as the rate is progressively increased eutectic appears in alloys farther to the left of S_1 or the right of S_2 . In such alloys the amount of liquid that attains the eutectic composition tends to be small, and in consequence films of the second constituent are generally formed instead of a true eutectic structure. In alloys that lie to the right of S_1 or the left of S_2 the amount of eutectic formed increases with the rate of cooling. The reason for this follows directly from the points considered in connexion with the solidification of a primary solid solution. In discussing this it was shown that in the range of solidification the amount of solid formed during each small drop in temperature decreases as the rate of cooling increases. In alloys that solidify as solid solutions this means that the range of solidification widens as the rate of cooling is increased. In alloys in which solidification is completed by the formation of eutectic it means that more liquid remains when the composition

of the liquid reaches the point E (or the area dEc). As this liquid solidifies as eutectic, it follows that the amount of eutectic increases with the rate of cooling. Summarizing the matter it may be stated, (1) that under equilibrium conditions only an alloy of composition E consists entirely of eutectic, while with accelerated cooling alloys that lie to the left and right of E can be caused to solidify as eutectic; (2) that in alloys farther to the right and left of E an increase in the rate of cooling is accompanied by an increase in the amount of eutectic and a decrease in the amount of primary crystals; and (3) that in alloys which are within the limits of solid solubility for equilibrium conditions eutectic appears when faster rates of cooling are employed.

EUTECTIC STRUCTURES

A variety of different structures are exhibited by eutectics. In any particular specimen containing primary crystals and eutectic the constituents in the eutectic are relatively small, but their size, like that of the primary crystals, is controlled by the rate of cooling through the range of solidification. In certain alloys the size of the constituents in the eutectic may also be influenced by the presence of other constituents (e.g. when sodium is added to aluminium-silicon alloys) or by treatments performed on the molten metal (e.g. in cast iron).

The solidification of alloys of eutectic composition begins at nuclei scattered throughout the melt. From each of these a eutectic grain develops and solidification is complete when contact is established between grains growing from different points. The alloy then consists of an aggregate of grains which are about the same size and shape and contain the same constituents in the same proportions and arranged in the same pattern. When primary skeleton crystals are already in existence before the eutectic change begins, the development of eutectic grains may still take place in the above way, or alternatively the formation of the eutectic may begin at the surfaces of the existing skeletons. Wherever the eutectic formation begins it tends to extend radially from this point forming eutectic grains. As far as the authors are aware only one investigator has actually observed successive stages in the solidification of an alloy consisting of primary skeleton crystals and eutectic. This was done by Boyles (594) who quenched small cast-iron melts into water from different temperatures in the range of solidification. As the portions that solidified before quenching could be distinguished from those that solidified during quenching it was thus possible to observe stages in the process of freezing. It was found, as would be expected, that skeleton crystals of the primary solid solution of carbon in iron (i.e. austenite) were formed first, then the formation of the eutectic began at points in the melt from which eutectic grains grew radially and independent of the skeletons until contact was established between them. Fig.132 illustrates the structure

at a stage when the development of the eutectic grains was well advanced. The white matrix is the metal that was still molten at the instant of quenching, the dark rosettes are the eutectic grains, and the small symmetrically arranged spots are sections of the primary skeletons. It will be seen that the eutectic grains grow radially and that their growth is not interfered with by the skeletons. This mode of growth

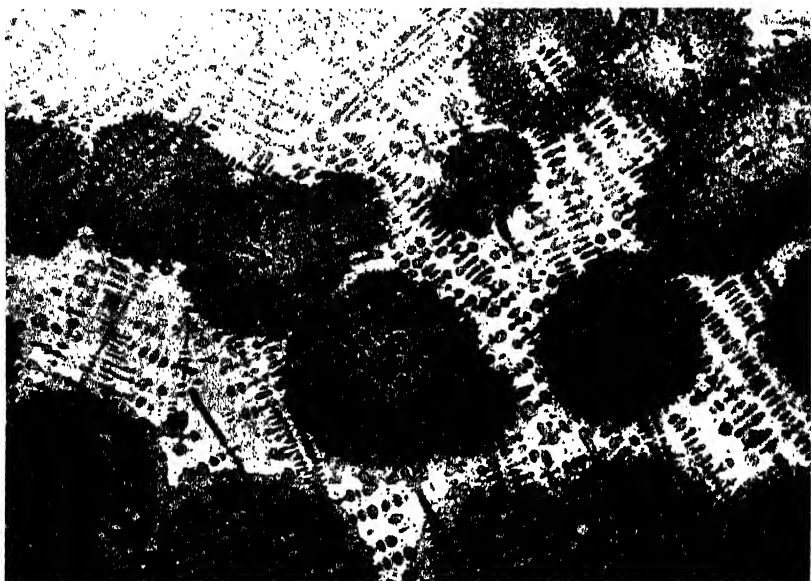


FIG. 132. Stage in the growth of eutectic grains. (Boyle, *Metals Technology*.)

of eutectic grains is probably quite common; but it does not always occur, for in many cases the formation of eutectic begins at the surface of existing crystals, and wherever it begins the subsequent growth is frequently confined to the spaces between the skeletons. In connexion with this last point the amount of primary skeleton crystals must be a factor of some importance, for the eutectic grains could hardly grow as shown in Fig. 132 if they were forming in small channels between skeletons that had developed until little liquid remained.

Having given a brief description of the growth of eutectic grains, the differentiation of the grains in a solid alloy may be considered. This depends to a pronounced extent on the nature of the eutectic under consideration, the method by which it is etched, and the magnification under which it is examined. In general, however, there are four ways in which one eutectic grain may be differentiated from another. It appears that in all eutectics one of the constituents forms a matrix in which the other is embedded. This effect is most marked when the volume occupied by the matrix constituent is considerably greater than that occupied by the other (e.g. in the copper-cuprous oxide eutectic in which

the metal forms 96 per cent. and the oxide 4 per cent.), but it becomes less marked as the relative proportions become more nearly equal. Furthermore, it appears that in a given eutectic grain the whole of the matrix constituent has the same crystallographic orientation, i.e. it forms one crystal. Thus the matrix of one eutectic grain differs from that of another in the same way as the individual crystals in a pure metal differ from each other. In order to observe this the eutectic must be suitably etched and examined under a low power, i.e. a magnification sufficient to reveal the eutectic grains but insufficient to distinguish the two constituents of the eutectic. A second factor that may enable one grain to be distinguished from another is variation in composition between the first- and last-formed parts of the grains. In an absolutely pure binary alloy the eutectic change is not accompanied by any selective freezing, i.e. the composition of the eutectic remains the same during the whole process of solidification. When, as is usually the case, other elements

present, selective freezing occurs, and the last-formed portion of a eutectic grain is of different composition from the first-formed. Furthermore, impurities not soluble in the constituents of the eutectic may be concentrated at the boundaries between the grains.

Little attention has been given to the study of eutectic grains as differentiated by the above methods, and eutectics are seldom etched or examined by methods that reveal the grains independently of the structure within them. Generally, eutectics are etched so as to differentiate the two constituents and examined at magnifications that reveal them. When this is done the grains may be distinguished when the eutectic has a regular structure, but not when the structure is irregular. In many eutectics the structure at the outside of the grains is much coarser than that in the interior and the separate grains may be distinguished in this way. Thus the coarse structure in the centre of Fig. 133 marks the boundaries of the three grains shown, and in Fig. 141 the individual grains are again distinguished by the coarser structure at the boundaries. This is the third way in which one eutectic grain may be distinguished from another. The fourth method depends on the variation in the orientation of the eutectic pattern between one grain and another. Examples of this are shown in Figs. 123, 125, and 135, and the basis of this distinction may be illustrated by means of the iron-iron carbide eutectoid known as 'pearlite' which resembles a eutectic in many respects and is rather more regular in



FIG. 133. Mg-Mg₂Cu eutectic. $\times 250$.
(*Journal of the Institute of Metals.*)

structure. This consists of alternate plates of iron and carbide, and the thickness of the plates decreases as the rate of cooling through the range in which they are formed increases. In a particular specimen the plates are about the same thickness in all the grains, but any



FIG. 134. Pearlite. $\times 820$.

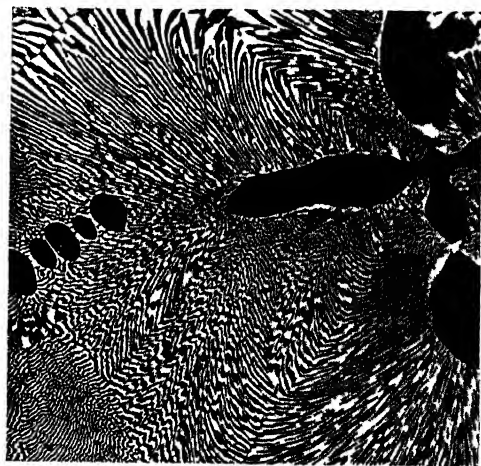


FIG. 135. Cu-Cu₃P eutectic. $\times 250$.

section prepared for microscopic examination cuts the plates in different grains at different angles. When the plane of the plates is exactly at right angles to the plane examined, the true thickness of the plates is observed, but the apparent thickness increases as the angle between the plane of the plates and the plane examined decreases. Thus when several grains of this eutectoid are obtained within a given field of view the structure observed is as shown in Fig. 134.

Attention may now be given to eutectic structures, i.e. the patterns formed by the two constituents. These patterns result from the way in which the simultaneous crystallization of the two constituents takes place, but very little is known about this process. The mode of formation of the eutectoid pearlite is described in Chapter XI where it is shown that the change takes place by the edgewise advance of the plates of iron and carbide. Certain eutectic structures appear to be formed in a similar way, but in general the factors that control the formation of eutectic structures are more difficult to understand. It appears in the

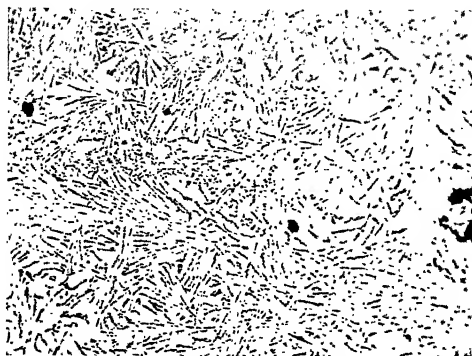


FIG. 136. 13 per cent. silicon, normal. $\times 75$.
(*Metal Progress.*)

first place that the matrix constituent may crystallize either radially from the point at which the eutectic change begins as illustrated in Fig. 132 or by the development of skeletons resembling those normally formed. The other constituents may crystallize quite independently of the matrix constituent and thus give rise to a eutectic which exhibits no pattern or in which the pattern depends entirely on the form adopted by the second constituent. Alternatively, the crystallization of the second constituent may be closely related to that of the matrix. Thus, when the matrix constituent grows radially, the second constituent may occur in the form of radiating rods or plates, whereas when it develops skeletons, the second constituent may be situated in the interstices of the skeletons giving rise to a kind of cellular structure. Eutectics have, however, been studied mainly as final structures and the way in which they form has received little attention. For the present it must therefore suffice to describe a few examples of these final eutectic structures.

In many eutectics one of the constituents crystallizes in much the same manner as if it were solidifying alone and the other simply constitutes the matrix. This occurs in the normal aluminium-silicon eutectic, i.e. when the change is not modified by rapid cooling or the presence of sodium. The silicon forms needle- or plate-like crystals and the aluminium fills the interstices. The resulting structure is shown in Fig. 136. Similar structures are realized in the iron-graphite

eutectic described in Chapter XIV, and in numerous aluminium-base alloys in which the second constituent of the eutectic is an intermediate constituent without very pronounced metallic properties, e.g. FeAl_3 , MnAl_6 , &c. When primary crystals of aluminium are present before the eutectic forms, the aluminium in the eutectic merges with these, leaving needles, plates, or small compact crystals of the other constituent in the interstices of the skeletons (Fig. 551). Similarly, when iron skeleton crystals are present before the iron-graphite eutectic forms, the

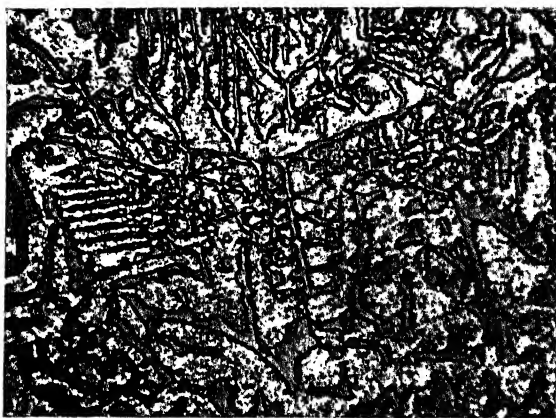


Fig. 137. Eutectic in Pb-Sn-Sb alloy. $\times 150$. (*Journal of the Institute of Metals*.)

iron in the eutectic merges with the existing crystals, leaving graphite flakes in between. In all these cases the character of the eutectic may be modified by rapid cooling and a more regular eutectic pattern is then produced.

In the examples described above, the constituent that crystallizes in its own way is of the type that does not form skeletons. In other alloys, however, certain eutectic constituents develop modified skeletons while the other constituent fills the matrix. Such a structure is shown in Fig. 137 taken from a paper by Weaver (80). It shows a eutectic of two constituents in one of the ternary lead-tin-antimony alloys. A similar eutectic is shown in Fig. 125. Eutectics of this type are comparatively common. They are known as 'Chinese-Script' and occur in such alloys as lead-bismuth, lead-antimony, &c.

In the remaining types of eutectics neither of the constituents forms definite crystals like the above. The two constituents crystallize together and combine to form a fairly regular pattern which, however, varies considerably in different alloys and in the same alloy under different conditions. Even in these eutectics one of the constituents usually forms the matrix and the other is distributed throughout it in the form of globules, rods, or plates. Examples of eutectics in which one of the constituents occurs as globules are provided by the cadmium-tin, copper-

silver, and copper-cuprous oxide eutectics. The first of these is illustrated in Fig. 138 (81). This type merges gradually into that in which one of the constituents occurs as rods, as in the iron- Fe_3C eutectic (Fig. 139) and the magnesium- Mg_2Cu eutectic (Fig. 123), and this in turn merges

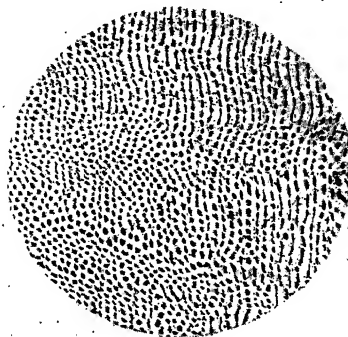


FIG. 138. Cadmium tin eutectic.
 $\times 165$. (*Journal of the Institute of Metals.*)

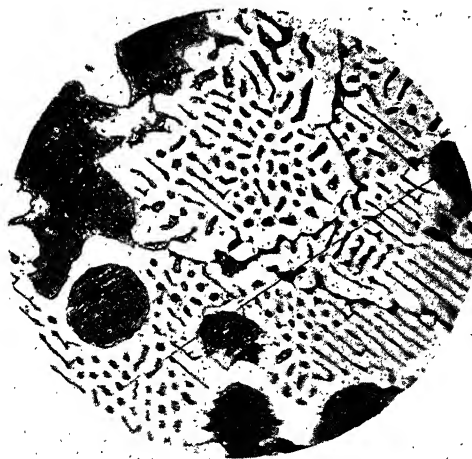


FIG. 139. Eutectic structure in iron-carbon alloys. $\times 820$.

into the type in which both constituents occur as plates, e.g. Fig. 135. There does not appear to be any fundamental difference between the three types of eutectics, in which one of the constituents occurs as globules or rods or both occur as plates. The apparent difference seems to be due to the surface tension and the time allowed for this factor to operate. Normally the two constituents in the eutectoid pearlite occur

in alternate plates as shown in Fig. 134, but if the metal is cooled extremely slowly the carbide may occur either as rods or globules distributed throughout a matrix of iron. Furthermore, after the lamellar structure is formed it may be converted to the other types by heating, and the

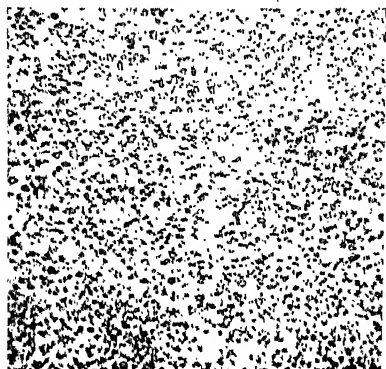


FIG. 140. Globularized pearlite. $\times 420$.

time required to accomplish this is greatly decreased if the eutectoid is subjected to mechanical deformation which breaks the brittle carbide plates. The resulting structure is shown in Fig. 140. Brady (82) has shown that the lamellar lead-tin eutectic (Fig. 141) may be globularized in a similar way. He has also shown, however, that even with rapid cooling the copper-silver eutectic is globular, and thus, although the above eutectics are related, alloys as ordinarily prepared generally display one definite type.

Thus far discussion has been confined to the shape of the particles of eutectic constituents. Attention may now be turned to their general arrangement in the grains. In eutectics of the types shown in Figs. 136 and 137 no definite eutectic grains can be recognized, but when fairly

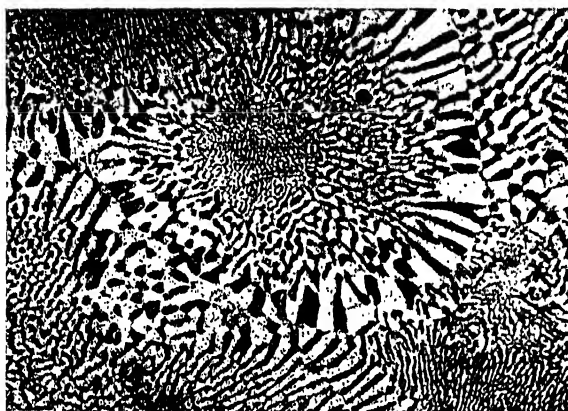


FIG. 141. Lead-tin eutectic. $\times 150$. (*Journal of the Institute of Metals.*)

regular patterns are developed the general arrangement of the particles in a grain is controlled by the directions in which it grows. Beginning from a point in the melt or on the surface of a primary crystal a eutectic grain grows by the simultaneous crystallization of the two constituents, and when these form plates or rods the directions of these are related to the directions of growth. This is dealt with in detail in Chapter XI in

connexion with the formation of eutectoids. In the meantime it will suffice to refer to Fig. 135 in which this relation between the eutectic structure and the directions of growth is clearly illustrated. When the alloy is exactly of eutectic composition and the grains grow from centres distributed throughout the melt each grain tends to develop a kind of radial structure like that shown by the lead-tin eutectic (Fig. 141). The radial structure is less well defined when primary crystals are present (Fig. 135), and it cannot be observed at all when the primary crystals are close together. Frequently the structure becomes coarser near the boundaries of the grains (e.g. in Figs. 133, 135, and 141) and this appears to be due to the retardation of crystallization by the heat evolved during the eutectic reaction.

Summarizing this short description of eutectic structures it may be said that there are two principal types: (1) that in which one of the constituents crystallizes more or less in the form it adopts when crystallizing alone, and (2) that in which the form of both constituents is determined by the fact that they crystallize simultaneously. In both cases, of course, the constituents crystallize simultaneously, but whereas the structure of eutectics of the second type is dominated by this condition that of eutectics of the first type is not. Eutectics of the first type can be further classified by distinguishing (A) those in which the constituent that crystallizes in its own way does not form the skeletons characteristic of metals from (B) those in which this constituent does form crystals resembling the skeletons characteristic of metals. Eutectics of the second type can be further classified according to the form of the particles of the constituents, viz. (A) globules, (B) rods, and (C) plates. As the eutectic solidifies after the primary crystals it forms the matrix of the alloy. Consequently, unless the amount of eutectic is very small it isolates the primary crystals from one another, i.e. the eutectic is continuous while the primary constituent is discontinuous. In every eutectic, however, one constituent forms a matrix for the other, i.e. in the eutectic itself one constituent is continuous and the other is not. From the point of view of response to deformation the continuity of a constituent is an important factor and is dealt with in the next chapter.

GENERAL CONSIDERATION OF STRUCTURES FORMED AT SOLIDIFICATION

Crystals of the common metals in a pure state grow by the formation of skeletons followed by the filling of the interstices as described at the beginning of this chapter. In the absence of other elements which may produce variations in composition within each crystal or form films outlining the branches of the skeletons, there is nothing to distinguish one part of a crystal from another. Consequently, when pure metals are etched and examined microscopically all that is observed is the difference between the crystals arising from their different orientations. Thus the

microstructures shown in Figs. 3 and 4 are obtained and the external shape of the crystals is determined by mutual interference.

If to a pure metal an element is added that is retained in solid solution, the process of selective freezing will tend to produce variations in composition in each crystal. A small amount of such an element does not produce observable variations, and thus, so long as the impurities are soluble in the solid, structures like those shown in Figs. 3 and 4 may be obtained even when the metal is comparatively impure. But the variations in composition within each crystal become more pronounced as the amount of the added element is increased, and the characteristic structure of a cast primary solid solution is as shown in Figs. 101, 102, 104. In such alloys the composition of each crystal varies progressively from the beginning to the end of solidification, but it is usually impossible to show this in a micrograph, and thus micrographs of these alloys give the impression that two different constituents are present. As the rate of cooling through the range of solidification is decreased the variations in composition arising from selective freezing become less pronounced. With sufficiently slow cooling homogeneous crystals may be obtained, but it is more usual to attain this result by moderately rapid cooling followed by prolonged heating below the temperature at which solidification is complete. This is known as annealing. If the treatment is performed on the cast alloy a considerable time is required to obtain homogeneity and the final structure is similar to that of a cast pure metal (Fig. 4). If, however, the cast metal is mechanically deformed so as to break down the original crystals before annealing, then homogeneity is obtained in a shorter time and the final structure may contain twinned crystals as shown in Fig. 93.

If an element that is not retained in solid solution is added to a pure metal, solidification begins with the crystallization of the metal and is completed by a eutectic reaction. If the solid solubility of the added element is negligible, the eutectic reaction will occur when only a very small amount is present. Under these conditions a eutectic structure is not produced because that portion of the basis metal that remains in the eutectic liquid is deposited on the existing primary crystals. The second constituent then appears in the form of films outlining the primary crystals. A very small amount of an insoluble constituent has a marked influence in this respect, and consequently, although Fig. 4 may be taken to represent the structure of a pure metal or of one containing a certain amount of soluble impurities, it does not represent that of a metal containing a small amount of insoluble impurities. Oxygen and lead are nearly insoluble in solid copper and iron in solid aluminium. In each case particles of the second constituent (i.e. lead, cuprous-oxide, or FeAl_3) appear when the element is present in amounts less than 0.05 per cent. These constituents tend to form isolated globules or particles rather than films, but in many commercially pure metals comparatively small amounts of insoluble impurities are so distributed as to outline the

skeletons. The effect of this is shown in Fig. 142 which is a micrograph taken by Weaver (83) of common tin (99.18 per cent. purity). The different crystals are distinguished by their colour and in each crystal the skeleton is outlined by the insoluble impurities. Very small amounts of impurities are sometimes capable of producing this effect and such structures are common in comparatively pure metals. At higher magnifications, when the amount of the impurities is very small, each crystal seems to be divided up into cells (the sections of the branches of the skeleton) by lines of impurities that can hardly be identified as such. These lines are sometimes called veins or sub-boundaries.

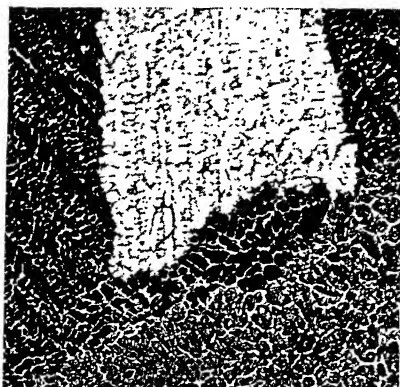


FIG. 142. Common tin. $\times 50$. (*Journal of the Institute of Metals.*)

As the amount of insoluble impurity is increased the amount of liquid that undergoes the eutectic reaction increases, true eutectic structures are formed, and the relative amounts of primary crystals and eutectic alter in the manner illustrated by Figs. 98, 99, and 100. When the added element is partially soluble in the basis metal, the structure of alloys within the limit of solubility is as described above in connexion with primary solid solutions. The structure of alloys beyond the limit of solid solubility is as described in connexion with insoluble additions. Consequently, the above general description of structures covers pure metals and alloys belonging to systems of Types 1, 2, 3A, and 3B except in those cases when one of the metals does not form skeleton crystals of the type characteristic of metals.

Some intermediate constituents form crystals similar to those of pure metals, while others form crystals of quite a different type. Furthermore, some intermediate constituents may vary considerably in composition while others are of fixed composition. Those constituents that form crystals of the skeleton type and vary considerably in composition resemble primary solid solutions. The others do not. A pure constituent of this latter type has a similar microstructure to a pure metal, for whatever may be the mode of growth of the crystals their external shape is

controlled in both cases by mutual interference. When, however, an intermediate constituent of this type occurs in association with a eutectic, the different mode of growth of the crystals results in a pronounced difference in the final structure. An example is shown in Fig. 143 which is a micrograph of an alloy containing 14.5 per cent. of antimony, 7.7 per cent. of tin, and 77.8 per cent. of lead (Weaver (83)). The little white cubes are a constituent SnSb which solidifies first and the matrix is the eutectic of SnSb and a solid solution of tin and antimony in lead (see also Fig. 137). Further examples of the types of crystals formed by



FIG. 143. Crystals of SnSb in
 $\times 150$. (*Journal of the Institute of Metals*.)

intermediate constituents when they are first to crystallize from the melt are shown in Figs. 144–6. These micrographs were taken by Gwyer, Phillips, and Mann (548) of complex alloys made by adding iron and copper, or silicon, iron and copper to aluminium. Fig. 144 represents an alloy containing 2 per cent. of iron and 40 per cent. of copper. The dark masses are primary crystals of CuAl_2 , the long white needles are primary crystals of an intermediate constituent of uncertain composition, and the eutectic consists of CuAl_2 and a primary solid solution based on aluminium. Fig. 145 represents an alloy containing 5 per cent. of silicon, 10 per cent. of copper, and 1 per cent. of iron. Again the dark crystals are CuAl_2 , the white needles are an intermediate constituent of uncertain composition, the half-tone crystals are silicon, and the matrix a primary solid solution based on aluminium. Fig. 146 represents an alloy containing 5 per cent. of silicon, 10 per cent. of copper, and 2 per cent. of iron. The dark crystals are again CuAl_2 and the half-tone silicon. The white matrix is the aluminium solid solution and the skeletons are an intermediate constituent forming a eutectic with aluminium.

In systems of Type 4 alloys that lie on the basis metal side of the eutectic crystallize by the growth of skeleton crystals and the subsequent formation of eutectic in the interstices. Alloys that lie on the other side of the eutectic solidify by the formation of crystals of the types described

above, followed by the eutectic reaction which, however, does not always result in a eutectic structure. It remains to describe the structures formed at solidification in systems of Type 5. A typical diagram for systems of the type is shown in Fig. 129. Alloys that lie to the left of b solidify by the formation of skeleton crystals of the primary solid

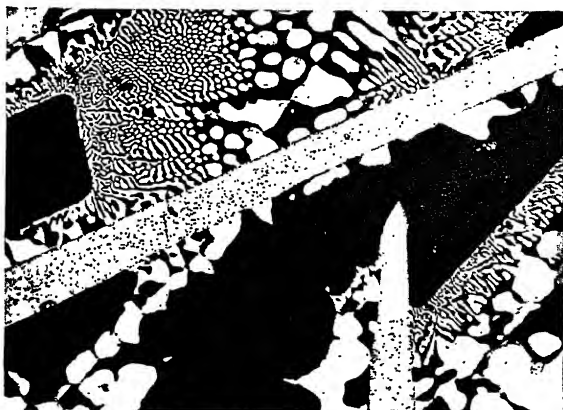


FIG. 144. Constituents in Al-Fe-Cu alloy. $\times 200$. (*Journal of the Institute of Metals*.)



145. Constituents in Al-Cu-Si-Fe alloy. $\times 200$. (*Journal of the Institute of Metals*.)

solution α . In such systems the β constituent frequently resembles a primary solid solution and therefore alloys that lie between c and e solidify in much the same way as those to the left of b . The γ constituent, however, is usually quite different from a primary solid solution and consequently alloys that lie to the right of f do not solidify by the formation of skeleton crystals. In alloys that lie between b and c two constituents are formed at solidification, viz. skeletons of α and a matrix of β . In alloys that lie between e and f two constituents are again formed,

but although the β forms skeleton crystals, the γ does not fill the matrix in the manner described above. It tends, rather, to form crystals of a characteristic shape so that the final structure consists of these crystals in a matrix of β . In alloy systems of Type 3c (Fig. 119) crystallization takes place in the manner described above for α , β , and $\alpha+\beta$ alloys in systems of Type 5.



FIG. 146. Constituents in Al-Cu-Si-Fe alloy. $\times 200$.
(*Journal of the Institute of Metals.*)

The foregoing brief description covers the general types of structure formed at solidification. After solidification, changes in structure may occur as a result of constitutional changes in the solid. Furthermore, these changes in structure and constitution are capable of being profoundly modified by controlling the rate of cooling, and this is accompanied by a pronounced alteration in properties. The changes in solid alloys are thus of scientific interest and practical importance, and the next chapter is devoted to their consideration.

CHAPTER VI

CONSTITUTIONAL AND STRUCTURAL CHANGES IN SOLID ALLOYS AND THE RELATIONS BETWEEN STRUCTURE, CONSTITUTION, AND PROPERTIES.

CHANGES IN PURE METALS

IN Chapter II (Table 8) seven metals that can exist in more than one crystallographic form are mentioned, namely, iron, cobalt, cerium, thallium, tin, manganese, and chromium. All these except thallium and cerium are comparatively common and the crystallographic changes they undergo are therefore important. In iron, cobalt, tin, and manganese the changes are more or less reversible transformations that take place during heating and cooling through certain ranges of temperature, but in chromium as ordinarily prepared and used the crystal structure is body-centred cubic at all temperatures, and the hexagonal form is peculiar to metal electro-deposited under certain conditions. The transformations undergone by iron, cobalt, tin, and manganese are as follows:

Iron

Below 906° C.	Body-centred cubic α
Between 906–1,403° C.	Face-centred cubic γ
Above 1,403° C.	Body-centred cubic δ

Cobalt

During cooling changes from face-centred cubic to close packed hexagonal at 403° C.

During heating changes from close packed hexagonal to face-centred cubic at 477° C.

Tin

Below 18° C.	Diamond cubic (Fig. 9). Grey tin. α
Between 18–161° C.	Body-centred tetragonal. White tin β
Above 161° C.	Close packed hexagonal. γ

Manganese

Below 742° C.	Cubic with 58 atoms per cell. α
Between 742° C. and 1,191° C.	Cubic with 20 atoms per cell. β
Above 1,191° C.	Face-centred tetragonal. γ

In iron and manganese the crystallographic changes occur at comparatively high temperatures and take place reversibly during heating and cooling. They do not take place, however, at the equilibrium temperatures given above, as even the slowest rates of heating and cooling that can be employed in studying them are too rapid to permit true equilibrium to be realized. Consequently, they occur at lower temperatures

during cooling and higher temperatures during heating, e.g. the change from α - to γ -iron takes place at 909°C . during very slow heating, and that from γ - to α -iron at 898°C . during very slow cooling. Like other changes, these transformations are affected to some extent by the rate of heating and to a still greater extent by the rate of cooling. This difference between heating and cooling arises from the fact that changes take place less rapidly at lower temperatures and more readily at higher temperatures, and while an increase in the rate of cooling tends to depress a transformation to a range of temperature in which it proceeds with greater difficulty, an increase in the rate of heating tends to raise it to a range in which it proceeds with more facility. The change from γ - to α -iron occurs at 898° during cooling at a rate of 2° per minute; it is lowered to 892°C . with a rate of cooling of 12°C . per minute, and is further lowered by a greater increase in the rate of cooling.

In cobalt and tin the transformations occur at lower temperatures and are not reversible to the same extent as those in iron and manganese. Thus the change from face-centred cubic cobalt stable at high temperature to close-packed hexagonal cobalt stable at low temperature is easily suppressed, and at atmospheric temperature the metal may have either crystal structure and both types may occur in the same sample. Furthermore, although white tin is not the stable form at temperatures below 18°C ., it requires prolonged exposure at temperatures considerably below this to produce the change to grey tin. It is this transformation that gives rise to the phenomenon known as 'tin-pest', for as a result of it the compact white tin changes into a grey powder.

Transformations from one crystal form to another are accompanied by physical changes. One of the most important of these is the thermal change which consists of an evolution of heat during cooling and an absorption of heat during heating. Another is the change in density, and it is by observing these that the temperatures of the transformations are detected. In iron the heat evolved or absorbed in the $\alpha \rightleftharpoons \gamma$ change is about 4.9 calories per gramme, and that in the $\gamma \rightleftharpoons \delta$ change is about 1.7 calories per gramme. The latent heat of fusion is about 64.9 calories per gramme. The density of α -iron at 20°C . is 7.8685. It decreases with rising temperature and is 7.5706 at 906°C . At this temperature the α -changes to γ -iron, which has a density of 7.6327 at 906°C . The transformation is therefore accompanied by a contraction during heating and an expansion during cooling. The density of γ -iron decreases with rising temperature and at $1,403^{\circ}\text{C}$. it is 7.4077. At this temperature it changes to δ with a density of 7.3900. Thus, this transformation is accompanied by an expansion during heating and a contraction during cooling.

When alloys are made by adding other elements to metals that undergo polymorphic changes, the conditions under which these take place are affected by the added elements, and the solubility of the added element in the basis metal is affected by the crystallographic changes. When carbon, nickel, manganese, copper, or cobalt are added to iron they tend

to increase the range of stability of the face-centred cubic γ -iron at the expense of the body-centred cubic α and δ forms, i.e. they raise the $\gamma \rightleftharpoons \delta$ change and lower the $\alpha \rightleftharpoons \gamma$ change. One result of this is that as the amount of these elements present in iron increases the $\gamma \rightleftharpoons \delta$ is raised until it reaches the melting-point, and thus alloys that contain more than a certain amount solidify in the face-centred instead of the body-centred form. This is shown for the case of nickel in Fig. 119. Point *h* represents the position of the $\gamma \rightleftharpoons \delta$ change in pure iron. When an alloying element is added this point becomes a range and the lines *hc* and *hd* show how the range is raised by addition of nickel. Alloys to the right of *d* solidify as solid solutions of nickel in γ -iron. Alloys to the left of *c* solidify as solid solutions of nickel in δ -iron. Similar conditions are realized in the alloys of iron with carbon, cobalt, manganese, and copper. As a result of the lowering of the $\gamma \rightleftharpoons \alpha$ change by these elements γ -iron is stabilized at temperatures below 906° C. The progressive addition of nickel, for example, lowers the change so much that when about 34 per cent. are present γ -iron is stable down to -100° C. The effect of manganese is similar, but cobalt does not begin to lower the $\gamma \rightleftharpoons \alpha$ change until about 45 per cent. are added, and although copper and carbon progressively lower the change, the extent to which this takes place is restricted by the limited solubility of these elements in γ -iron.

Chromium, silicon, phosphorus, tungsten, molybdenum, vanadium, and aluminium tend to increase the range of stability of the body-centred cubic α - and δ -iron at the expense of the γ -iron, i.e. they lower the $\gamma \rightleftharpoons \delta$ change and raise the $\alpha \rightleftharpoons \gamma$ change. When a sufficient amount of any of these elements is added, the $\gamma \rightleftharpoons \delta$ and $\alpha \rightleftharpoons \gamma$ transformations meet, no γ -iron is formed, and as there is no distinction between α and δ the alloys undergo no allotropic changes during heating and cooling. The broken loop at the left-hand side of Fig. 128 represents the lowering of the $\gamma \rightleftharpoons \delta$ and the raising of the $\alpha \rightleftharpoons \gamma$ change with increase in the phosphorus content. At 0.5 per cent. of this element these changes meet and no solid solutions based on γ -iron occur in binary alloys containing more than this amount. The broken line in Fig. 128 is known as the γ -loop, and γ -iron is stable within it. The amounts of the various elements required to close the loop, i.e. to suppress the formation of γ -iron are, chromium 12.8 per cent., vanadium 1.1 per cent., silicon 2.5 per cent., tungsten 6.6 per cent., molybdenum 4 per cent., aluminium 1 per cent., and phosphorus 0.5 per cent. When iron is alloyed with several elements some of which tend to increase and others to decrease the range of stability of γ -iron, then these elements tend to counteract each other. This is discussed in Chapter XII in connexion with the iron-chromium-carbon and iron-chromium-nickel ternary systems.

Just as the addition of other elements affects the crystallographic changes, so these changes affect the solid solubility of the added elements in the basis metal. In the case of iron the elements that increase the range of stability of γ -iron are more soluble in this than in α - or δ -iron.

The reverse is true for the elements that decrease the range of stability of γ -iron. Carbon belongs to the former group and the pronounced difference in its solubility in γ - and α -iron respectively is of great importance in relation to the heat-treatment of steel. This, and related factors, are considered in detail in later sections of this chapter.

When a crystallographic change takes place in a solid metal it involves an alteration in the arrangement of the atoms in space. The atoms do not, however, disappear from one set of positions and reappear in others, nor do they temporarily become disordered while one space-lattice is breaking up and another is being formed. Actually one crystal form changes to another by a gradual movement of the atoms relative to each other without any intervening disordered state. It is certainly difficult to obtain direct evidence of what occurs during such a change, but in the case of the $\alpha \rightleftharpoons \gamma$ inversion in iron (and certain other similar

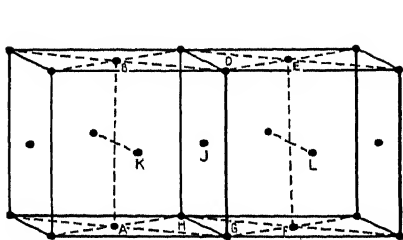


FIG. 147.

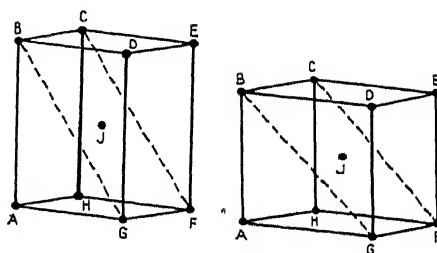


FIG. 148.

changes that occur in alloys) intermediate stages in the change can be retained, and if the original, the final, and intermediate states are known, the general features of the transformation may be inferred. These are described as follows by Bain (84). Two unit cells of face-centred cubic γ -iron are represented by the full lines in Fig. 147. If the lattice points are connected up as shown by the broken lines a body-centred tetragonal lattice is formed. $ABDGHCEF$ is one unit cell and J is the body-centred atom. Thus the face-centred cubic lattice is also a body-centred tetragonal lattice for which the axial ratio is 1.414. At the temperature of the $\gamma \rightleftharpoons \alpha$ transition the cube edge of the γ -lattice is 3.529 Å., therefore the dimensions of the unit tetragonal cell $ABDGHCEF$ are $AB = 3.592$ Å. and BC and $BD = 2.54$ Å. At the transition temperature the cube edge of the body-centred α -iron is 2.90 Å., and the transformation from γ - to α -iron takes place by a change in the dimensions of the unit body-centred tetragonal cell. This change is illustrated in Fig. 148. The side AB of the unit tetragonal cell shortens from 3.592 Å. to 2.90 Å. and the sides BD and BC lengthen from 2.54 Å. to 2.90 Å. In other words, the transformation from γ - to α -iron involves a compression of the lattice in the direction AB and its expansion in the directions BD and BC . The atoms do not alter their positions relative to each other; only the distances between their centres are changed. The net result is an increase

in volume. In the reverse change from α - to γ -iron the process described above takes place in the opposite direction and is, of course, accompanied by a decrease in volume.

The body-centred cubic lattice of α -iron may be regarded as a body-centred tetragonal lattice with an axial ratio of 1. If, by expansion in one direction and contraction in the other two, this ratio changes to 1.414 then the lattice points may be considered to form a body-centred tetragonal or a face-centred cubic lattice. In other words, both cubic lattices are particular forms of the body-centred tetragonal. While one form is changing to the other, however, the axial ratio is neither 1 nor 1.414, and therefore while the iron is transforming, its lattice is tetragonal and not cubic. This change does not take place, however, by a gradual transition from one lattice to another which proceeds simultaneously throughout a specimen. The change from γ to α begins at certain points and spreads from them until the whole specimen is converted. It cannot be said that there is at any time an appreciable amount of iron which forms neither a face-centred nor a body-centred cubic lattice. Increasing the rate of cooling depresses the transformation and causes it to proceed more rapidly, but it does not alter the fact that at any instant only a few atoms are actually changing their positions and no intermediate type of lattice is actually formed. Thus it is impossible to obtain pure iron in an intermediate state.

Carbon is soluble to an appreciable extent in γ -iron but is almost insoluble in α -iron. When a solution of carbon in γ -iron is cooled moderately slowly, the change from γ - to α -iron is accompanied by the deposition of carbon from solid solution in the form of Fe_3C . Increasing the rate of cooling depresses the $\gamma \rightarrow \alpha$ change in such a solid solution to a much greater extent than in pure iron, and by means of rapid cooling it is possible to lower it to below 400°C . It is then impossible for the carbon to be precipitated from solution in the time available, and the result is that when the specimen reaches atmospheric temperature the lattice change in the iron has taken place but the carbon still remains in solution. Owing to the presence of the carbon, however, the lattice cannot change completely to the body-centred cubic form, and consequently the iron is retained in a condition intermediate between the face-centred and body-centred cubic, viz. the tetragonal form. It is to be expected that the deviation from the body-centred cubic lattice should increase with the amount of carbon retained in solid solution, and in practice it is found that as the carbon content is increased from 0 to 1.4 per cent. the sides BD and BC (Fig. 148) decrease from 2.861 Å. (the length of the side of the unit cube of pure α -iron at atmospheric temperature) to 2.840 Å. while the side AB increases from 2.861 Å. to 3.034. In other words, the unit cell is intermediate between the two shown in Fig. 148, but as the axial ratio (1.068 with 1.4 per cent. of carbon) is much nearer 1 than 1.414, it is customary to regard the lattice as a slightly modified form of the α -iron lattice.

The plane $BCGF$ (Fig. 147) is a (111) plane in the face-centred cubic lattice and a (110) plane in the body-centred tetragonal lattice. It is also a (110) plane in the body-centred cubic lattice (Fig. 148). The same applies to the other (111) planes in the face-centred lattice, i.e. those parallel to $DEAH$, $BDHF$, and $CEAG$, and in general all the (111) planes in the face-centred lattice become (110) planes in the body-centred lattice. As, however, there are six sets of (110) and only four sets of (111) two sets of (110) in the body-centred cubic do not correspond with (111) in the face-centred. These are the sets parallel to $CHDG$ and $BAEF$ in the body-centred cube (Fig. 148) and they correspond with (100) planes in the face-centred cube. By joining the lattice points in Fig. 147 in different ways different body-centred tetragonal cells may be derived from the face-centred cubic lattice. In this figure as drawn $BUED$ is the top face of the unit tetragonal cell, but the lattice points could also be connected so that $KDLG$ was the top face, and if another two unit face-centred cubes were drawn in front of those shown it would be seen that GJD and the lattice point in the additional cells corresponding to J may also become a top face. From one face-centred cubic lattice three differently oriented body-centred tetragonal lattices and therefore three differently oriented body-centred cubic lattices may be derived. In each case one cube face in the body-centred is parallel to one in the face-centred lattice and all the (111) planes in the face-centred become (110) in the body-centred lattice. The other two cube faces in the body-centred are parallel, however, to (110) planes in the face-centred lattice and two (110) in the body-centred do not correspond with (111) in the face-centred lattice.

As already explained, the $\gamma \rightarrow \alpha$ transformation begins at certain points in the γ -iron crystals and these bear the same relation to the polymorphic transformation as nuclei do to solidification. They are usually situated in the boundaries of the γ -iron crystals and from each of them a crystal of α -iron grows. The manner in which this crystallization takes place in pure iron at 906°C . cannot be directly observed, but the way in which it takes place in iron-carbon alloys has been studied (see Chapter XI) and there is evidence that it proceeds in much the same way in the absence of carbon. During slow cooling which permits the transformation to take place in a range of temperature not far below 906°C ., the α -iron crystals assume rounded shapes, and Fig. 149 may be taken to represent a stage in the transformation of γ -iron (black) to α -iron (white). As the rate of cooling is increased, the α -iron crystals exhibit a tendency to grow preferentially along the (111) planes in the γ -iron and Fig. 150 shows this. This tendency for the α -iron to form needle- or plate-like crystals parallel to the (111) planes in γ -iron increases with the rate of cooling, which, of course, lowers the temperature of the transformation and causes it to be spread over a longer range. In general the change begins at several points in each crystal of γ -iron and the number of such points increases with the rate of cooling. This deter-

mines the number of crystals formed in the first instance, but as only three different orientations of α -iron can be produced from each crystal of γ -iron, it follows that adjacent crystals will frequently have the same orientation and will therefore coalesce when contact is established. Thus the number of α -iron crystals that can be distinguished when the trans-

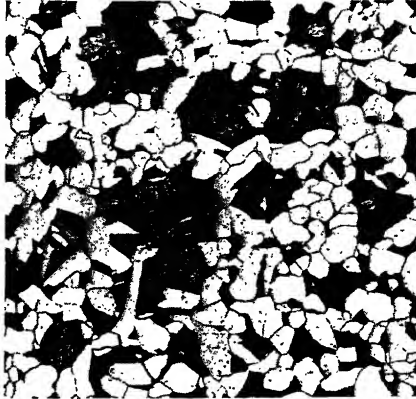


FIG. 149. α -Fe (white) forming from austenite (black). $\times 100$.



FIG. 150. α -Fe (white) forming from austenite (black). $\times 820$.

formation is complete will be smaller than the number of crystals that existed at an intermediate stage in the transformation.

The tendency for α -iron to form as plates parallel to the (111) planes in the γ -iron is also exhibited when the rate of cooling is very slow or the crystals of γ -iron are large. This will be explained in Chapter XI. In the meantime it is sufficient to note that this tendency is shown when the rate of cooling is accelerated and to consider the reason for the formation of these plates. The α -iron crystals tend under suitable

conditions to extend along the (111) planes in the γ -iron because this is the direction in which they can develop most easily. As the (111) planes in the γ -iron become (110) planes in the α -iron it may be said that the (110) planes in the α -iron are directions of easy growth. In other words, the requisite change in the position of the atom takes place most readily on these planes. The lattice points B, C, G, F , and J (Figs. 147 and 148) lie on a (111) plane in γ -iron and a (110) plane in α -iron. In both cases the arrangement of the atoms is the same but the spacing is different. It is

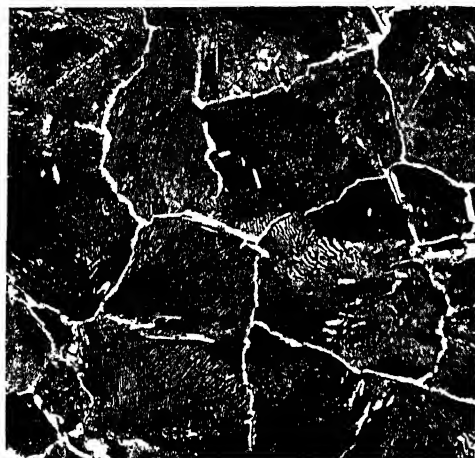


Fig. 151. Boundary films of Fe_3C . $\times 250$.

a simple movement, however, from the relative positions occupied by B, C, G, F , and J in the left-hand sketch in Fig. 148 to those occupied in the right-hand sketch. Thus (111) planes in γ -iron readily become (110) planes in α -iron, and α -iron crystals tend to develop along these planes when the conditions are such that they must take advantage of possible directions of easy growth. These conditions arise when the change is caused to take place rapidly by accelerating the cooling or when the slow removal of heat or carbon from the surfaces of growing crystals encourages growth in the form of plates.

Conditions like those described above are realized during many changes in solid alloys. According to the alloy and the conditions under which the transformation occurs, massive crystals like those shown in Fig. 149 or plate-like crystals like those shown in Fig. 150 may be formed. Furthermore, intermediate types may be produced, and sometimes the constituent is deposited in the form of envelopes round the crystals of the parent constituent as shown in Fig. 151.

The crystallographic changes described above are the most important changes that occur in solid pure metals. They are accompanied by changes in numerous properties and affect the behaviour of alloys which contain metals that undergo them. In addition, however, some

pure metals undergo magnetic transformations, and these are not associated with crystallographic changes. Thus, iron, nickel, and cobalt are ferromagnetic below and paramagnetic above 768°, 340°, and 1,100° C. respectively. The magnetic change in α -iron at 768° C. is accompanied by a pronounced thermal change, but electrical resistivity, specific volume, &c., are not affected. Before the crystal structure of iron at different temperatures had been determined (1921) there was some difference of opinion as to whether the non-magnetic α -iron that exists between 768° and 906° should or should not be regarded as a separate modification β . The view generally accepted, however, is that different modifications have different crystal structures, and as there is no change in crystal structure at 768° C. the β form of iron is no longer recognized. The same applies to nickel and cobalt. There is no connexion between magnetic transformations and different modifications, and although the effects of alloying elements on magnetic change points are indicated by lines in constitutional diagrams they have quite a different meaning from true phase boundaries.

DIFFUSION

Solid diffusion, i.e. the migration of atoms through a solid, is one of the most important metallurgical phenomena. It is involved in most of the changes that occur in solid alloys, and it is also a feature of many processes and operations. In the remaining chapters of this book many examples of diffusion will be described, and it is therefore appropriate that a brief account of its general features should be given here.

No diffusion is involved in polymorphic changes in pure metals such as have just been described, and in certain changes in alloys, e.g. the formation of martensite, it does not occur. On the other hand diffusion is the only phenomenon involved in the homogenization of primary solid solutions. In describing the solidification of these it was explained that the solid diffusion which proceeds concurrently with selective freezing tends to eliminate the variations in composition resulting from the latter process, but in practice the rate of cooling through the range of solidification is not slow enough to permit this to proceed to the extent necessary to prevent heterogeneity. As a result the crystals of primary solid solutions vary in composition between the first skeletons and the last-formed matrix. If, however, the solid solution is maintained at (or subsequently heated to) a temperature just below that at which solidification is completed, then migration of the atoms will proceed in the crystals until a uniform distribution of the two components is attained. This is one of the changes that occurs in solid alloys and it depends only on diffusion. Most of the other changes described in this chapter involve diffusion and the formation of new crystals. Thus changes in solid solubility (next section) involve the formation of new crystals by the component rejected from solid solution, but the rate at which these grow depends on the rate at which the precipitating solute can diffuse.

Similar conditions arise in changes from one constituent to another, and also in eutectoid changes, where the principal difference is that two constituents are being formed at once. Changes in atomic arrangement, i.e. in the distribution of two sorts of atoms between the lattice points of a common lattice, do not involve diffusion in the sense of migration, but they depend on the same ultimate phenomenon, namely, the interchange of positions between neighbouring atoms.

As diffusion proceeds with time at a rate that depends on temperature, any change that involves diffusion is affected to a pronounced extent by those factors. A newly-solidified solid solution alloy is not in equilibrium if the two components are unevenly distributed in the crystals. A condition of equilibrium or stability means that no change takes place with time, and we have seen that in such an alloy solid diffusion tends to take place in order to bring about a uniform distribution of the components. The time required for this result to be attained is a minimum at a temperature just below that at which solidification is completed. It increases as the temperature decreases, and may become infinitely long below a certain temperature. If, therefore, an alloy is cooled at a rate that does not allow any substantial amount of diffusion to occur at high temperature, it may be retained unchanged down to a temperature at which no diffusion can occur. Such an alloy is then stable in the sense that it does not change with time, but the stability is due to the fact that the change cannot take place under the conditions in which the alloy is maintained. The tendency to change is there and the rapidly-cooled alloy is in a different condition from one that was permitted to become homogeneous at high temperature before cooling. This retention at a low temperature of a condition that existed at a high temperature by cooling at a rate that prevents diffusion is a most important phenomenon, and is the basis of the heat-treating operations described at the end of this chapter. In this connexion it is necessary to distinguish between true stability which implies no tendency to change, and the condition in which there is a tendency to change (suggesting instability) and an absence of actual change (suggesting stability). For this purpose the term 'persistence' may be used.

Changes in solid alloys involve diffusion of the components of the alloys from one point to another within them. Diffusion is also involved, however, in a number of processes in which the composition of a metal or alloy is altered by causing some element or elements to diffuse into or out of it. In the carburizing of steel, for example, the carbon content at the surface is raised by causing carbon to diffuse into the steel. In nitriding, nitrogen is caused to diffuse in a similar way, and in other processes zinc, aluminium, and chromium are caused to diffuse into the surface of steel. On the other hand, the removal of gases from metals by heating *in vacuo* depends on the diffusion of these gases to the surface of the metal. In addition to these intentionally performed operations in which diffusion is concerned there are numerous other

examples of the incidental effects of diffusion. When, for example, steel is heated in certain types of atmosphere (Chapter X), carbon is removed from the surface, and further amounts then diffuse to the surface and are in turn removed. Again, when copper is heated in atmospheres containing hydrogen, this gas diffuses into the metal and combines with copper oxide to form water-vapour which embrittles the metal, and finally the properties of steel are adversely affected under certain conditions by hydrogen diffusing into the metal during pickling (Chapter X) or heat treatment (Chapter XII).

Most of the above-mentioned examples of phenomena or processes in which diffusion is involved are considered in detail in later sections. Meanwhile, attention may be given to some aspects of diffusion considered as a general phenomenon. Even in a pure metal a type of diffusion occurs. Although metal crystals have so far been described as if each atom remained stationary at a fixed lattice point and no interchange of positions occurred, it must now be pointed out that the positions assigned to atoms are mean positions about which they vibrate, and now and again this vibration results in changes in position between neighbouring atoms. This phenomenon which is known as 'self-diffusion' cannot be experimentally observed when all the atoms in a pure metal are the same, but an opportunity of observing it is provided by the fact that the atoms of the radioactive isotope of lead are similar to those of lead except for their radioactivity. By studying the diffusion of radioactive lead through ordinary lead, von Hevesy was able to determine the rate of 'self-diffusion'. This interchange of position between atoms in a pure metal is clearly the basis of the diffusion of solute atoms through a solvent, and it reveals that the conditions in solid metals at atmospheric temperature are not so static as is sometimes supposed. Raising the temperature increases the amplitude of the atomic vibrations. This results in an increase in the rate at which interchange of lattice positions proceeds, and this in turn leads to an increase in 'self-diffusion' and ordinary diffusion.

The diffusion of atoms through a solid metal indicates some degree of solid solubility of these atoms in the metal, and it may be supposed that atoms that are completely insoluble in a metal will not diffuse through it. It is doubtful, however, whether complete insolubility is ever realized, and as the rate of diffusion does not decrease with the solid solubility, but appears rather to increase as the solid solubility decreases, it may be assumed that diffusion may occur even when no solid solubility can be measured. The actual mechanism of migration then depends on whether the diffusing (or solute) element forms a substitutional or an interstitial solution with the matrix (or solvent) metal. In the former case the solute atoms occupy positions on the solvent lattice and take part in the normal interchanges of positions between neighbouring atoms. In this way they migrate through the lattice. In the case of interstitial solutions the solute atoms migrate through the

interstices between the solvent atoms. Here again, of course, the migration is associated with the atomic vibrations, and the solute atoms jump from one position to another and do not glide freely through the solvent. As the solid solutions of metals in metals are of the substitutional type, the mechanism of diffusion associated with this is characteristic of the diffusion of metals. Interstitial solutions are formed when elements like carbon, nitrogen, and hydrogen are dissolved in metals, and the mechanism associated with this is characteristic of gaseous diffusion.

In general, diffusion always tends to take place in such a way that a uniform distribution of the solute will be attained. The reason for this is presumably that the presence of the solute atoms decreases the stability of the lattice in their vicinity and increases the number of interchanges in which they are involved. Consequently, the solute atoms will always tend to migrate from regions where they are more to regions where they are less concentrated. This leads to consideration of the factors that influence the rate at which atoms of one kind diffuse through a lattice composed of atoms of another. One important factor in this connexion is the degree of difference between the atoms concerned. Thus, as shown by Mehl (595), the slowest rate of diffusion in lead is exhibited by the radioactive isotope of lead, and the rate of diffusion increases from tin, through thallium, bismuth, cadmium, and silver to gold, i.e. it increases with the difference between the element concerned and lead. Quoting unpublished work, this author also states that the rate of diffusion in copper increases from zinc, through aluminium and silicon, to tin. In the first example the rate of diffusion of the elements increases as their solid solubility in lead decreases. The same applies in the second example for the metals zinc, aluminium, and silicon, but tin does not fit in with this arrangement because its generally accepted solubility in copper is greater than that of aluminium or silicon. It is not to be expected that the rate of diffusion of different elements in a common solvent would in all cases be inversely related to their solid solubility, for while some factors which favour large solubility lead to slow rates of diffusion other factors will have the reverse effect. It is interesting to note, however, that similarity of the atoms, which leads to extensive solid solubility, tends to be associated with slow diffusion. This suggests that diffusion is promoted, as stated above, by the instability resulting from the presence of solute atoms. The more these differ from the solvent atoms the greater will be their effect in causing instability and the greater will be the tendency of the lattice to keep rejecting them from given positions until a uniform distribution results.

Other factors that influence the rate of diffusion at a given temperature are the size of the solute atoms, and the melting-point of the solvent. In general, the rate of diffusion through a given solvent will tend to increase as the size of the solute atoms decreases. Furthermore,

the rate of diffusion of a given solute in different solvents will tend to increase as the melting-point of the solvent decreases. This is supported by direct experiment and also by general observations on the behaviour of alloys. Thus, precipitation-hardening changes which depend on diffusion occur in lead-base alloys at temperatures below atmospheric, in aluminium-base alloys at atmospheric temperature, and in copper- and iron-base alloys at elevated temperature.

The simplest case of diffusion is provided by a sheet of metal on each side of which a fixed but different concentration of the solute atoms is maintained. Under these conditions the amount of solute diffusing through the sheet will depend on the nature of the solvent and solute respectively, the temperature, and the difference in concentration on the two sides of the sheet. In most actual examples of diffusion, however, complicating conditions are introduced. In the homogenizing of a solid solution, for instance, the concentrations at the ends of the diffusion gradient are continually changing, with the result that the rate of diffusion becomes slower and slower as equilibrium is approached. In the case of a gas diffusing into a metal the concentration of the diffusing atoms at the metal surface may be kept constant and the concentration at the innermost limit of diffusion will be constant, and zero for a certain time. This innermost limit will, however, move progressively until it reaches the middle of the sheet (supposing diffusion to be taking place from both sides), thereafter the concentration of gas at the lower limit of the diffusion gradient will begin to increase.

Again, a simple case of diffusion requires that the diffusing element shall be in the atomic state and that nothing shall impede its movement. When we are dealing with constitutional changes in alloys these conditions are realized, but the same does not apply when diffusion into a metal from an external source is concerned. If the substance diffusing from the external source is a metal which has been plated, rolled, or solidified on to the solvent metal, the atomic condition is fulfilled, but diffusion may be impeded by the absence of perfect contact or the existence of an oxide film on the surface of the solvent. If the substance diffusing from the external source is a gas, then (except in such special cases as that of hydrogen liberated at the surface of metal immersed in acid) the required atomic condition will not be fulfilled; and the gas molecules will have to be dissociated at the metal surface before diffusion can occur. This dissociation is produced by activated adsorption on the surface of the metal, and in general the diffusion of gases into metals is controlled by adsorption. As adsorption is a specific phenomenon (i.e. certain metals adsorb certain gases), the diffusion of gases into metals is also specific, and while nitrogen, which is adsorbed by iron and chromium, diffuses into these metals, it does not diffuse into copper on which it is not adsorbed. Furthermore, as adsorption is affected to a pronounced extent by the condition of the metal surface, the diffusion of gas into metal is also affected by this.

As explained in Chapter II the activity of a metal surface is increased by roughening either mechanically, by etching, or by alternate oxidation and reduction. This increases its capacity for adsorbing gas and also the rate at which the gas diffuses into the metal. Thus Smithells (11) shows that etching the surface of iron with dilute nitric acid increases the rate of diffusion of hydrogen to ten times that of its diffusion into iron with a polished surface.

The rate of diffusion of metals into metals increases with the temperature, and the rate of diffusion of gases increases with the temperature and the pressure. This behaviour of gases is not what would be expected in view of the dependence of diffusion on adsorption, for as explained in Chapter II activated adsorption reaches a maximum at comparatively low temperatures and then begins to decrease. Furthermore, pressures of the order of one atmosphere are sufficient to cover metal surfaces with an adsorbed layer. It might be inferred from this that increasing the temperature above that of the maximum on the adsorption curve or increasing the pressure above that required to complete the adsorbed layer would not be accompanied by an increase in the rate of diffusion. As pointed out by Smithells and Ransley, however, adsorption measurements are made on finely-powdered metals and the decrease in adsorption above a certain temperature may be due to sintering (i.e. coagulation or welding together of the particles) which decreases the available surface. As diffusion experiments are performed with sheet metals this factor does not interfere, and adsorption appears to increase progressively with temperature. This does not mean that the adsorbed layer becomes thicker, but simply that it is maintained while diffusion into the interior of the metal is taking place. With regard to the effect of pressures above those required to maintain the adsorbed layer, Smithells explains that the rate of diffusion at higher pressures depends mainly on the impact of molecules from the gas phase on the atoms adsorbed on the surface. If the impinging molecules have sufficient energy, the adsorbed atom may acquire the energy necessary to penetrate the surface, and the rate of diffusion will continue to increase with the pressure even after adsorption is complete.

The diffusion of gases into metals has so far been considered as if the only factors involved were the gaseous atmosphere, the adsorbed layer, and the underlying metal. These are the conditions realized when the gas concerned is hydrogen, but when oxygen and nitrogen are involved, the formation of compounds at the surface has to be considered. As explained in Chapter II only the residual affinities of the surface layer of metal atoms are involved in adsorption, but when the conditions relating to the gas, metal, temperature, and pressure are such that the affinity of the gas atoms for the metal atoms exceeds that of the metal atoms for each other, then a compound is formed on the surface. Thereafter, the gas reaching the metal surface must diffuse through the film of oxide or nitride, and when it has done so it may either combine to form

another layer of compound under the first or be available for diffusing into the metal. Under such conditions the compound will be in equilibrium with a certain concentration of gas atoms in the layer of metal in contact with it, i.e. any tendency for the concentration of gas atoms to exceed the equilibrium value will be counterbalanced by the formation of more compound, and any tendency for it to fall below this value will be counterbalanced by reduction of some of the compound. It is the concentration of the gas atoms in the metal in contact with the compound that is concerned in diffusion, and as this is not affected by the gas pressure on the outer surface of the compound the rate of diffusion is independent of pressure.

The diffusion of metals into metals has so far been considered as if only primary solid solutions were formed, but actually, when one metal is in contact with another under conditions that permit diffusion, all the constituents that these two metals can form may be produced. In the alloys of copper and zinc for example (Chapter XV) six constituents are formed, i.e. primary solid solutions in each of the metals and four intermediate constituents. When zinc is diffusing into copper, layers of all these may be produced in addition to layers of mixed constituents, and the process of diffusion is complicated by the equilibrium between the different constituents. Some simple examples of the conditions that arise when diffusion is accompanied by the formation of new constituents are considered in later chapters, i.e. in Chapter X in connexion with the decarburization of steel, and in Chapter XIII in connexion with carburization.

It remains to consider the effect of grain boundaries and cold-working on diffusion. As explained in Chapter II the packing of the atoms in the immediate vicinity of crystal boundaries cannot be so orderly as elsewhere, and the boundaries must therefore be regarded as regions of relative instability. Because of this it may be expected that diffusion would proceed more readily along grain boundaries than through the lattice of the crystal itself. This has been shown to occur in certain cases, but it is not a general rule. An example of preferential diffusion along crystal boundaries is provided by the diffusion of thorium in tungsten which has been the subject of several investigations. Here it has been shown that the rate of diffusion decreases rapidly with increase in the crystal size of the tungsten and that diffusion through a single crystal is extremely slow. It has been calculated that in this case the rate of diffusion along a grain boundary is one hundred times faster than through a grain. Similar results have been obtained for the diffusion of molybdenum in tungsten, and it has been shown that it is ten times faster in a sample consisting of small crystals than in a single crystal. Other cases in which diffusion has been shown to take place preferentially along the grain boundaries are: carbon in tungsten, where the rate of diffusion in fine-grained metal is four times as rapid as in a single crystal; copper in zinc, where the rate of diffusion in an

aggregate is six times as rapid as in a single crystal; and copper in iron. On the other hand, zinc does not diffuse preferentially along the grain boundaries of copper, nitrogen and carbon do not diffuse preferentially along the grain boundaries of iron, nor does hydrogen diffuse preferentially along the grain boundaries of iron or nickel. It has been shown in fact that the diffusion of hydrogen through iron and nickel is independent of the crystal size and that it proceeds in a single crystal of iron just as rapidly as in an aggregate.

It will be seen from the above that preferential diffusion along the grain boundaries is characteristic of some combinations of solute and solvent but not of others. There are, however, a number of cases in which diffusion proceeding through the crystal lattice produces effects only observed at the boundaries. Thus, when steel is immersed in acid, atomic hydrogen is liberated at its surface and some of it diffuses into the metal. It appears that this diffusion proceeds through the crystal lattice, but it has the effect of producing a tendency to fracture at the grain boundaries. Again, when copper is heated in an atmosphere containing hydrogen it becomes susceptible to intercrystalline fracture. In this case the brittleness is due to the intercrystalline cohesion being weakened by the pressure of water-vapour resulting from the combination of the hydrogen and copper oxide. The effect is produced at the crystal boundaries because it is there that the copper oxide is situated. When solid metals are oxidized it is sometimes found that under the layer of oxide formed on the surface there is a region in which oxide is formed along the grain boundaries. This suggests that in certain cases oxidation proceeds preferentially along the boundaries. It has been shown, however, that the diffusion of oxygen through oxide films is sometimes much more rapid along the boundaries of the oxide crystals than through their lattice. Furthermore, it has been shown that the boundaries of the oxide crystals correspond to those of the underlying metal crystals. It follows therefore that the preferential penetration of oxide along the boundaries of the metal crystals may be due to the fact that those are the points to which oxygen has easiest access and not to preferential diffusion there.

Cold-working has the effect of decreasing the stability of the crystal lattice and may therefore be expected to facilitate diffusion. Quantitative proof of this is difficult to obtain, however, for in general the temperatures at which rates of diffusion can be measured are higher than those at which recrystallization occurs. It has been shown, however, that cold-working a single crystal of tungsten increases the rate of diffusion of thorium to that characteristic of an aggregate. Furthermore, many changes in alloys which involve diffusion are known to be promoted by cold-working, and although such effects cannot be measured in terms of diffusion rates they are well known and of great importance. In concluding this section on diffusion it should be added that an excellent survey of metal in metal diffusion is given by Mehl

(595) and a similar review of gas in metal diffusion by Smithells (11). These publications should be consulted for fuller information and for references to the data on which this section is based.

CHANGES IN SOLID SOLUBILITY

In Chapter V attention was confined to the mutual solubility of metals at the temperature of solidification, but in many systems changes in solid solubility occur during subsequent cooling. Such changes do not, of course, occur in systems of Type 1 (Table 24) in which neither metal is soluble in the other to a measurable extent, nor do they take place in systems of Type 2 in which the two metals are mutually soluble in all proportions. In systems of Types 3A, 3B, and 4, however, changes in solid solubility are the rule, and changes of a closely related character occur in systems of Types 3C, 3D, and 5. These latter are, however, more correctly described as transformations from one constituent to another and are dealt with separately in the next section.

In systems of Types 3A, 3B, and 4 the changes that occur during cooling almost invariably involve a diminution in solid solubility. In systems of Type 3A the solubility of each metal in the other decreases as indicated by the lines S_1K_1 and S_2K_2 in Fig. 117, while in those of Types 3B and 4 the solubility of one metal in the other decreases as indicated by the line bd in Fig. 128. By way of illustration, the copper-silver system is reproduced in Fig. 152. Under equilibrium conditions alloys that lie to the left of S_1 (8.8 per cent. Cu) solidify as primary solid solutions of copper in silver, and those that lie to the right of S_2 solidify as primary solid solutions of silver in copper. After solidification, however, the solubility of copper in silver decreases as shown by the line S_1K_1 and that of silver in copper as shown by line S_2K_2 . If an alloy containing exactly 8.8 per cent. of copper solidifies under equilibrium conditions, it consists entirely of the primary solid solution α at 779.4° C. As soon as it is cooled below this temperature, however, it begins to change, and if the rate of cooling is slow enough to permit equilibrium to be maintained, the α solid solution changes in composition along S_1K_1 and the excess copper is precipitated as the solid solution β . Thus, whereas all the copper (8.8 per cent.) is dissolved in the silver at 779.4° C., only 5.6 per cent. remains in solution at 700° C., and as the temperature continues to fall at the equilibrium rate the amount of copper dissolved in silver decreases as follows: at 600° C. 3.3 per cent.; at 500° C. 1.9 per cent.; at 400° C. 1 per cent.; at 300° C. 0.6 per cent.; and at 200° C. 0.4 per cent. The remainder of the copper is precipitated as the solid solution β which also changes in composition along the line S_2K_2 . Thus at 300° C. the alloy containing 8.8 per cent. of copper consists of α solid solution containing 0.6 per cent. Cu and β solid solution containing 0.3 per cent. Ag in such proportions that the amount of α is to the amount of β as de is to dc .

If the alloy contains less than 8.8 per cent. of copper, e.g. 5 per cent., the change in the α primary solid solution does not begin immediately the alloy is cooled below 779.4°C . In this particular alloy, represented by X (Fig. 152), solidification is complete at 860°C . and no change occurs until it is cooled to 680°C ., then the α solid solution becomes supersaturated with copper and some β solid solution is precipitated. As cooling is continued the α solid solution changes in composition along the line S_1K_1 , the amount of β increases and this changes in composition

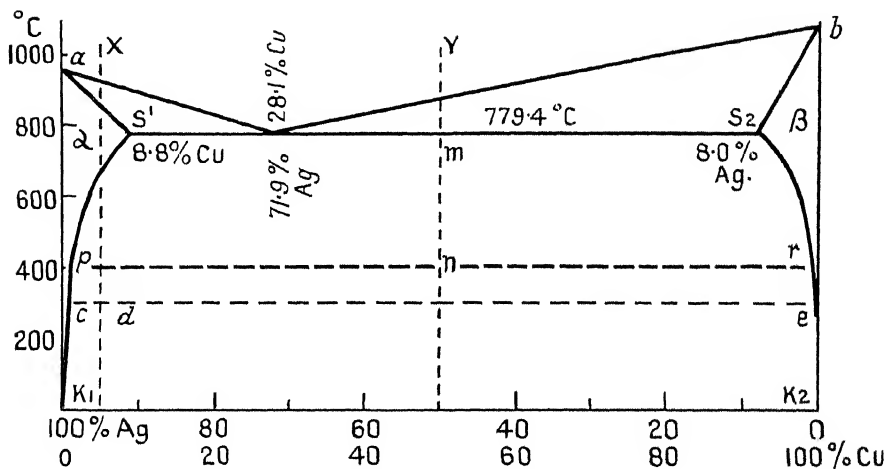


Fig. 152. The copper-silver system.

along the line S_2K_2 . Similar changes occur in alloys at the other side of the system which contain 8.0 per cent. of silver or less. Intermediate alloys containing between 8.8 per cent. Cu and 8 per cent. Ag solidify as mixtures of two solid solutions containing 8.8 per cent. Cu and 8 per cent. Ag respectively. As the temperature falls both solid solutions change in composition along the lines S_1K_1 and S_2K_2 . Since the slopes of these are very similar the changes in the composition of the two solid solutions are not accompanied by a pronounced alteration in the relative amounts. Thus in the alloy Y the proportions at solidification are given by the ratio—amount of α is to amount of β as mS_2 is to mS_1 , i.e. 50.48 per cent. α and 49.52 per cent. β . At 400°C . the proportions are in the ratio of nr to np , i.e. 50.25 per cent. α and 49.75 per cent. β . The change that takes place is therefore mainly diffusion. Copper diffuses from α to β and silver from β to α . Thus α becomes poorer in copper and richer in silver and changes along S_1K_1 , while β becomes poorer in silver and richer in copper and changes along S_2K_2 . If the two lines had different slopes there would be a greater change in the relative amounts of the two constituents. If, e.g., the solubility of silver in copper did not alter with falling temperature then copper could not diffuse from α to β and

silver would not diffuse from β to α . In this case the entire change in the composition of α would be produced by the formation of more β . This is the condition realized in systems of Types 3B and 4 (Table 24).

As an example of the changes in solid solubility that occur in systems of these types the alloys of aluminium and copper may be described. The requisite portion of the diagram is shown in Fig. 153. In the proportions of 54 per cent. Cu and 46 per cent. Al (by weight) these two metals form an intermediate constituent CuAl_2 which melts at 594°C ., does not dissolve either of its components, and has a tetragonal crystal

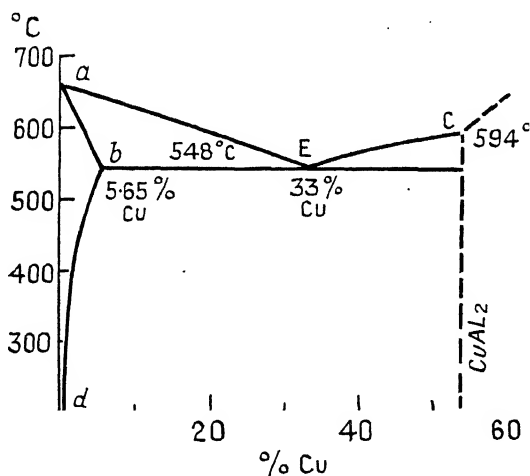


FIG. 153. The aluminium-copper system.

structure, $a = 6.054 \text{ \AA}$. and $c = 4.864 \text{ \AA}$., with 12 atoms (8 Al and 4 Cu) per unit cell. At the temperature of solidification aluminium dissolves 5.65 per cent. of copper and the eutectic between this solid solution and CuAl_2 occurs at 33 per cent. of copper. Below 548°C . the solubility of copper in aluminium decreases as shown by the line bd and at various temperatures the amounts soluble are as follows: at 500°C . 4.15 per cent.; at 400°C . 1.45 per cent.; at 300°C . 0.7 per cent.; at 200°C . 0.5 per cent. An alloy containing 5.65 per cent. Cu solidifies as a primary solid solution. As soon as it cools below 548°C . it becomes supersaturated with copper, and as the temperature falls the composition of the solid solution changes along bd while the excess copper is precipitated as CuAl_2 . Alloys containing less than 5.65 per cent. Cu have to be cooled below 548°C . before the change in the solid solution begins. Thus one containing 2.65 per cent. Cu does not become supersaturated until cooled to 450°C ., and one containing 0.5 per cent. Cu not until cooled to 200°C . Alloys containing more than 5.65 per cent. Cu solidify as primary crystals of the solid solution containing 5.65 per cent. Cu in a matrix of the eutectic of this and CuAl_2 . As they are cooled the composition of the solid solution alters and this applies to that in the eutectic as well as the

primary crystals. Since the composition of the CuAl_2 does not alter, all changes in the composition of the solid solution involve the formation of more CuAl_2 .

Attention may now be turned to the structural aspects of the constitutional changes described above. In alloys that lie between S_1 and S_2 (Fig. 152) both constituents exist when the alloys have newly solidified. One of the constituents is only present in the eutectic; the other exists in the eutectic and also forms primary crystals. As already stated, owing to the similar slopes of the lines S_1K_1 and S_2K_2 changes in composition are not accompanied by marked changes in the relative amounts of α and β . All that takes place is diffusion of copper from α to β and of silver from β to α . Thus the change in constitution is not accompanied by a change in structure. In alloys that lie between b and E (Fig. 153) both constituents are present in the newly solidified alloy. During subsequent cooling no change takes place in the CuAl_2 , which is present in the eutectic, but the solid solution changes in composition and the copper rejected goes to form more CuAl_2 . According to the diagram an alloy containing 10 per cent. Cu consists at 548°C . of 84.1 per cent. primary crystals of the solid solution and 15.9 per cent. eutectic, which in turn consists of 43.43 per cent. solid solution and 56.57 per cent. CuAl_2 . At 200°C . this same alloy contains 70.77 per cent. of primary crystals and 29.23 per cent. of eutectic which in turn contains 39.25 per cent. solid solution and 60.75 per cent. CuAl_2 . If the composition of the eutectic remains constant at 33 per cent. Cu, the proportion of eutectic therefore increases from 15.9 to 29.23 per cent. during cooling from 548° to 200°C . and at the same time the percentage of CuAl_2 in the eutectic increases from 56.57 to 60.75. Under these conditions the most important change in structure would be the increase in the amount of eutectic. But there is no evident reason why the composition of the eutectic should remain constant while the changes under discussion are taking place, so that, instead of the precipitated CuAl_2 leading to the formation of more eutectic it may go to increase the amount of CuAl_2 in the eutectic, viz. by thickening the existing lamellae or by forming boundaries of CuAl_2 between the eutectic and the primary crystals.

Alloys at the sides of the systems under consideration solidify as primary solid solutions without eutectic and the changes in solid solubility lead to the appearance of new phases at a lower temperature. Thus the alloy X (Fig. 152) solidifies as α solid solution. When it is cooled to 680°C . some β begins to form and when it reaches 200°C . it contains about 9.7 per cent. of this. There are no β -crystals formed at solidification on which the β formed in the solid can precipitate, and consequently there is a definite change in structure resulting from the appearance of this new phase, and its distribution is controlled by different factors from those pertaining to structures formed at solidification. Similar conditions may be realized in alloys that contain both phases at solidification when the rate of cooling is not sufficiently slow

to permit the rejected constituent to diffuse into the existing crystals. Thus, whereas the adjustments in the composition of α and β in alloy *Y* (Fig. 152) are brought about almost entirely by diffusion during very slow cooling, they involve the precipitation of α at other points during more rapid cooling. The whole question of the structures resulting from changes in solid solubility is closely connected with the effect of the rate of cooling, and further consideration will be deferred until this has been dealt with. Meanwhile, attention may be given to the mechanism of precipitation from solid solutions.

In liquid solution the atoms are in continual movement and the conditions under which the precipitation of a solid begins are as described in connexion with the appearance of nuclei in molten metals. At temperatures above that at which solidification begins, the atoms of the constituent that will later be precipitated make frequent contacts, but exhibit little tendency to combine. As the temperature is lowered the tendency to combine increases and small crystal fragments are temporarily formed. Further lowering of the temperature leads to an increase in the stability of these, and finally they become sufficiently stable to become permanent nuclei for continued crystal growth. Thus in crystallization from liquid solutions the factors concerned are the movement of the atoms and the forces of attraction. In solid solutions, however, the atoms of the dissolved constituent are not continually moving in the solvent, and the part played by the forces of attraction is obscure. Therefore the beginning of precipitation from solid solution involves different factors. The subsequent growth of the crystals is, however, much the same in both cases.

Between 860° and 680° C. the alloy *X* (Fig. 152) is (under equilibrium conditions) a homogeneous solid solution of copper in silver. At 680° it becomes supersaturated with copper, and as a result minute crystals of β make their appearance at certain points. At this temperature the 5 per cent. of copper is uniformly distributed throughout the whole alloy, but at 670° C. the major portion of the alloy contains 4.7 per cent. while certain small areas contain 96.2 per cent. There is no change in space-lattice to consider, for both constituents are face-centred cubic. The required change may therefore be brought about by diffusion. The diffusion concerned is 'counter-current', i.e. copper diffuses from α to β and silver from β to α . This is easily conceived when α and β are coexistent and changing in composition together. But what steps are involved in the first appearance of β ? Whenever the unchanged α is cooled below 680° C. it becomes supersaturated with copper, and it is in accordance with the diagram that copper should diffuse away from it while silver diffuses into it. In the absence of β , however, where does the copper go to or the silver come from? Evidently α cannot change its composition until β appears. But β cannot appear until the copper content at some points is raised to 96 per cent. and this involves diffusion of copper to these points and of silver away from them. Thus the β cannot form until

the α changes its composition, and it is clear, therefore, that the two changes must begin simultaneously with the appearance of an infinitely small amount of β and an infinitely small change in the remaining α . These simultaneous changes take place under equilibrium conditions, but when these are departed from, alterations in the mechanism of the change may be expected. These are dealt with in a later section.

Similar conditions to those described above are realized when the precipitation of CuAl_2 begins in an alloy containing less than 5.65 per cent. of copper (Fig. 153). In this case, however, the formation of the CuAl_2 involves a change from a face-centred cubic to a complex tetragonal lattice with 12 atoms in the unit cell. Three changes must therefore take place simultaneously: (1) diffusion of copper away from, and of aluminium into, the regions where the solid solution will remain; (2) diffusion of copper to, and of aluminium away from, the points where CuAl_2 will form; and (3) a change in space-lattice when CuAl_2 is formed. After the above described changes have begun they proceed in much the same way as those involved in solidification. In alloy *X* (Fig. 152) the β -crystals grow at the expense of α by a process of 'counter-current' diffusion, and in aluminium-copper the CuAl_2 crystals grow at the expense of the solid solution as a result of a similar process, i.e. copper diffuses to the surface of the growing crystals and builds them up while at the same time aluminium diffuses away.

The term counter-current diffusion used in connexion with the above changes describes accurately enough what takes place, but it is evident that there must be some difference between the movement of atoms of the solute and solvent metals respectively. During the formation of CuAl_2 , copper is gradually withdrawn from all over the solid solution to build up the crystals of this compound which grow as the temperature falls. In moving from one point to another the copper atoms must make their way through the aluminium lattice and this is diffusion. To take up the lattice points vacated by copper atoms in the solid solution and reduce the aluminium content at the surface of the growing CuAl_2 , movement of aluminium atoms must also take place, but this does not involve diffusion of aluminium atoms through the aluminium lattice in the same sense as the movement of copper atoms does. In both cases the movement is a step-by-step process. An aluminium atom in the neighbourhood of a lattice point vacated by a copper atom takes up this vacant position. Its position is in turn taken up by another adjacent atom and so the process continues until a vacant place is left near the CuAl_2 to be taken up by a copper atom. The same applies to the copper atoms which move step by step taking up positions vacated by other atoms. Nevertheless, the copper atoms move through the aluminium lattice while the aluminium atoms may be said rather to adjust their positions. The difference is slight but as a result of it the movement of the atoms of the basis metal is frequently ignored. Thus the growth of CuAl_2 crystals is said to involve the diffusion of copper

atoms to their surface, and the growth of β solid solution from α solid solution in a silver-copper alloy is said to involve the diffusion of copper towards the β .

Rather different conditions are involved when the solid solution concerned is of the interstitial type. When, e.g., Fe_3C is being precipitated from a solid solution of carbon in γ -iron, the carbon atoms that diffuse from the solid solution to the growing crystals of Fe_3C do not leave vacant lattice points. In this case, therefore, all that takes place is a contraction of the iron lattice to fill the blanks left by the carbon atoms. Such movement of the iron atoms as takes place bears no resemblance to diffusion and consequently no counter-current diffusion accompanies this change. We may say, therefore, that the above described movement of the copper atoms in aluminium is diffusion, that the movement of the iron atoms during the formation of Fe_3C is not, and that the movement of the aluminium atoms during the formation of CuAl_2 does not come into either category.

The Effect of Time and Temperature on Changes in Solid Solubility.

Changes in the solid state are affected by under-cooling to a much greater extent than changes from liquid to solid. During extremely slow cooling they may begin at the equilibrium temperature, but as the rate of cooling is increased they are progressively lowered. Furthermore, their progress is affected by time and temperature. Diffusion is involved, and this proceeds at a rate that depends on temperature and to an extent that depends on time. Thus the amount of a new phase formed in a given range of temperature tends to decrease with the time taken to cool through it, and the time taken for a given amount of the new phase to form tends to increase with falling temperature.

If no other factors intervened a progressive increase in the rate of cooling would have the following effect on the formation of CuAl_2 in an alloy containing 5.65 per cent. of copper. During cooling at the equilibrium rate the changes would take place as represented by Fig. 153. An increase in the rate of cooling would depress the beginning of the change from 548°C . to, say, 500°C . The formation of CuAl_2 would then begin at a lower temperature and proceed in a range of temperature in which it could take place with less facility. Furthermore, the time taken to cool through this range would be less than when slower cooling was employed. The net result would be a substantial decrease in the amount of CuAl_2 formed during cooling to atmospheric temperature. A further increase in the rate of cooling would have a further effect in this direction, and therefore a progressive increase in the rate of cooling would progressively depress the beginning of the change and decrease the amount of CuAl_2 formed. Sufficiently rapid cooling would entirely suppress the change.

For two reasons, however, the effect of a progressive increase in the rate of cooling is not as simple as described above. In the first :

once the alloy under consideration is cooled below 548°C . the solid solution becomes supersaturated with copper. As cooling continues without a change taking place the degree of supersaturation increases, and the tendency for precipitation to occur also increases. Thus each successive equal increase in the rate of cooling tends to be accompanied by a smaller increase in the amount of under-cooling. This would not be of much importance if each successive equal increase in the rate of cooling was accompanied by a proportionate diminution in the amount of CuAl_2 formed. But as the tendency for precipitation to occur increases, the number of centres at which it begins also increases. This has the effect of reducing the distances over which diffusion has to take place, and consequently enables a greater amount of CuAl_2 to be formed while cooling through a given temperature interval at a given rate.

If the factors just described are neglected, it appears that increasing the rate of cooling in successive equal steps should result in decreasing the amount of CuAl_2 formed by progressively greater steps. Owing to the fact that the tendency for precipitation to begin increases with the degree of supersaturation, and that when it begins it proceeds more rapidly by starting at a greater number of centres, different results are obtained. Increasing the rate of cooling in successive equal steps results, in the first place, in decreasing the amount of CuAl_2 formed by progressively smaller steps. The factors that cause this are, however, only operative up to a certain rate of cooling. This is the rate that lowers the beginning of the change to such a temperature that even the increased number of centres is not enough to counterbalance the effects of slow diffusion at low temperatures and the short time available for it to take place. When this rate is exceeded further increase in the rate of cooling is accompanied by a rapid decrease in the amount of CuAl_2 formed, and ultimately by the complete suppression of the change. Thus the effect of the rate of cooling is not progressive. Below a certain rate of cooling the effect of a given increase is less than it is when that rate is exceeded. It should be noted that similar conditions do not arise in the case of changes that do not involve diffusion. The change from $\gamma \rightarrow \alpha$ -iron may be depressed by increasing the rate of cooling but there is no limit to the rate at which it can proceed once it begins. Thus, whereas rapid cooling may lower this transformation and spread it over a range of temperature it cannot be suppressed.

In order to obtain equilibrium conditions in changes that occur in solids, long periods of time are required, and these increase as the temperature falls. Most methods of cooling give rise to conditions such that a longer time is occupied in cooling through each successive equal decrement of temperature. But this increase in the time taken to cool through equal temperature intervals is small in comparison with the decrease in the rate of diffusion. Thus, with a given rate of cooling, the precipitation of CuAl_2 from solid solution in aluminium may follow the line *bd* (Fig. 153) down to 500°C . Then if the cooling is not retarded in some

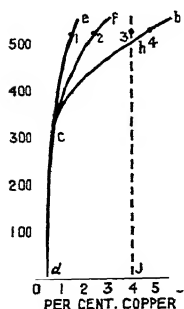
way the amount of CuAl_2 formed will decrease, i.e. the change in the composition of the solid solution will follow a line lying on the right of bd . This may continue down to 400°C . when CuAl_2 will cease to form, i.e. below this temperature the composition of the solid solution will not alter. Under these conditions the effects of increased supersaturation and the number of points at which precipitation is taking place do not arise. These only become important when the initial precipitation is depressed, i.e. with rates of cooling faster than those under consideration.

As a result of the sluggishness of solid solubility changes and the increase of this with falling temperature, great care is required in determining solid solubility curves. The method employed is known as 'bracketing'. In order to determine one point on the curve a series of specimens in which the composition varies in small steps is heated at the required temperature for a length of time considered sufficient to reach equilibrium. The specimens are then quenched and examined microscopically. Those in which no precipitate phase can be seen are within the limit of solid solubility at this temperature. The first specimen in which some precipitated phase is detected is outside this limit. Thus, one point on the solid solubility curve is determined with a degree of accuracy that depends on the smallness of the difference in composition between the various specimens in the series and the care with which they are examined for evidence of a precipitated phase. In determining the solid solubility of copper in aluminium Dix and Richardson (85) used 8 series each containing 6 specimens, and as the approximate position of the line bd (Fig. 153) was already known, the range of composition covered by each series varied according to the temperature from which it would be quenched. All the specimens were then heated just below the eutectic temperature for 11 days and one series was quenched. Then the temperature was allowed to fall slowly to 520°C . and maintained there for another 11 days when another series was quenched. This process was repeated at various other temperatures down to 200°C . Then all the specimens were examined and the line bd (Fig. 153) drawn between those that showed a small amount of CuAl_2 and those that showed none.

Most of the important binary alloy systems have been the subject of several investigations, and in general the solid solubility line is displaced towards lower solubility as the care taken in determining it is increased. Owing to the long times of heating employed to reach approximate equilibrium, it is evident that the closer the line gets to true equilibrium the farther it departs from what is realized in practice. Thus, whereas the amount of copper soluble in aluminium at 200°C . is 0.5 per cent., under equilibrium conditions considerably more is retained in solution by the methods employed in cooling castings and forgings.

The solution of CuAl_2 during heating is affected by the rate of heating, but owing to the fact that the rate of solution increases with temperature, the beginning of the change cannot be raised by rapid heating to the same extent as the reverse change can be depressed by rapid cooling.

The progress of the change is, however, affected to a pronounced extent by the rate of heating and the time for which the alloy is maintained at constant temperature. Suppose a copper-aluminium alloy containing 4 per cent. of copper is cooled under equilibrium conditions so that only 0.5 per cent. of copper remains in solution at atmospheric temperature. On heating again the precipitated CuAl_2 will begin to dissolve just above 200°C . The first stage in the process is that copper goes into solution in the aluminium in immediate contact with CuAl_2 , and there is no reason to suppose that the composition of the aluminium in immediate contact with CuAl_2 does not change in composition along the line db (Fig. 153).



. 154.

This, however, has little to do with the amount of CuAl_2 dissolved, for the composition of the solid solution in immediate contact with CuAl_2 may be altered as indicated by the line db by the solution of a negligible amount of CuAl_2 . What controls the amount dissolved is the extent to which copper diffuses throughout the whole of the solid solution. The line db (Fig. 153) is reproduced in Fig. 154. As the 4 per cent. alloy is heated, the solid solution in contact with CuAl_2 changes in composition along this line. As the distance from those surfaces of contact increases, the amount of copper in the solid solution decreases. Thus the line ce (Fig. 154) may be taken to represent the change in composition of the regions in the solid solution most remote from particles of CuAl_2 . Intermediate regions will contain intermediate amounts of copper, and the line cf may therefore be taken to represent the average copper content of the solid solution. The difference between these three lines depends on the extent to which the copper from the CuAl_2 diffuses throughout the solid solution. If the rate of heating is very slow a fairly uniform distribution of copper is maintained at all temperatures, i.e. the lines ce and cf lie very close to cb . The solution of CuAl_2 is completed when the line cf meets the line hj and when the heating is very slow this occurs just above h . As the rate of heating is increased, the lines ce and cf swing away from cb , i.e. more pronounced composition gradients are formed in the solid solution and less CuAl_2 is dissolved. In practice alloys are not heated at rates that permit equilibrium to be approximately realized. They are heated to a temperature above h at a convenient rate and maintained there until solution is complete. If, e.g., the alloy containing 4 per cent. of copper is heated to 520°C , i.e. to point 3, then on reaching this temperature the composition of the solid solution varies from 4 to 1, the average copper content is 2 and a considerable amount of CuAl_2 remains undissolved. While the alloy is maintained at 520°C diffusion takes place in the solid solution and CuAl_2 dissolves. Eventually equilibrium is established when the solid solution is uniformly of composition 3 and all CuAl_2 is in solution.

Fig. 154 may be taken to represent what occurs throughout the alloy. Alternatively, it may be taken to represent what occurs in the neighbourhood of one particle of CuAl_2 . The line ce indicates the copper content of the regions most remote from contact with CuAl_2 and their actual distance from particles of this compound depends on its distribution. If it occurs as large particles widely spaced, the copper from each particle has to diffuse throughout a large volume of solid solution; if it is distributed as small particles close together, the copper from each particle has only a short distance to diffuse. Clearly the copper content of the regions most remote from CuAl_2 will depend on their distance from particles of CuAl_2 , as well as on the rate of heating. Thus, with a given rate of heating the line ce (and therefore cf) approaches more closely to cb as the size of the particles of CuAl_2 decreases and their distribution becomes more uniform. Furthermore, the time required to bring about complete solution at 520°C . decreases as the size of the particles decreases and the uniformity of their distribution increases. In other words, the time needed to effect a uniform distribution of copper in the solid solution depends on the temperature and the distances over which diffusion must take place. These distances decrease with the particle size of the compound as long as the particles are more or less uniformly distributed throughout the alloy. Similar considerations apply to all alloys of the types under discussion, i.e. Types 3A, 3B, and 4, and their bearing on the heat-treatment of alloys will be dealt with in a later section.

Returning to the effect of the rate of cooling, it was explained in the previous section that under equilibrium conditions the change in the composition of the solid solution and the first appearance of the precipitating phase occur simultaneously, and that thereafter the two changes proceed concurrently as indicated by the constitutional diagram. It has just been shown, however, that the beginning of the change may be depressed by increasing the rate of cooling, and when this happens the conditions represented by the diagram are departed from. Thus, the diagram does not indicate that a solid solution containing 4 per cent. of copper in aluminium may be retained unchanged below 500°C . Experience shows, however, that it can be so retained down to any temperature by sufficiently rapid cooling. Furthermore, the diagram does not show what degree of stability will be displayed by the solid solution when retained unchanged below 500°C . Experience shows, however, that it changes slowly at atmospheric temperature, more rapidly at higher temperatures, more slowly at lower temperatures, and not at all at -80°C . It is evident that we are now dealing with conditions that are not represented by the diagram. This indicates the ultimate state that must be reached before equilibrium is attained at any temperature, but it does not show whether and at what temperatures an unstable state may persist nor at what rate a state that does not persist will change to a more stable one. Furthermore, the diagram does not explain what

kind of changes will occur when a solid solution decomposes at temperatures lower than those shown. When, e.g., a copper-aluminium alloy is retained at atmospheric temperature with substantially more than 0.5 per cent. of copper in solid solution the change that occurs is quite different from that which takes place during cooling at the equilibrium rate. Similar conditions arise in nearly all alloys and they will be considered in detail in later sections.

Structures Resulting from Changes in Solid Solubility.

When an alloy belonging to a system of Type 3A, 3B, or 4 contains both phases at solidification, the additional amount of one phase which results from the changes in solid solubility is precipitated on existing crystals of this phase during slow cooling. When, however, an alloy solidifies as one phase, the change in solid solubility leads to the appearance of a new phase at lower temperature. There are no existing crystals on which it may precipitate, and consequently the distribution of this phase and the form of the crystals depend on certain factors pertaining to structural changes in the solid. Similar conditions may be realized in alloys that contain both phases at solidification when the rate of cooling is not sufficiently slow to permit the precipitating constituent to diffuse to the existing crystals.

In so far as constitutional changes in the solid result in diffusion between existing constituents or the deposition of a new phase on existing crystals, the structures formed are simply modifications of those formed at solidification. When, however, a new phase appears in the solid or when a phase is deposited at points remote from existing crystals, then different kinds of structures are produced. The factors that influence the formation of these are quite different from those that operate during solidification, and in general, the most important are (1) the boundaries of the crystals of the basis solid solution, (2) the crystallographic planes in these crystals, (3) the surface tension of the precipitating phase, and (4) diffusion in the solid. A fifth important factor is introduced when the alloy is subjected to mechanical deformation while the constitutional change is in progress. During operations such as rolling and forging performed on the hot metal, the crystals of the precipitating phase are continually being broken up, those of the basis solid solution are being deformed, and new crystals are growing as a result of recrystallization. As the boundaries of the crystals of the basis solid solution frequently exert a pronounced influence on the distribution of the precipitating phase, the deformation and recrystallization of these combine with the breaking up of the crystals of the new phase in affecting its distribution. The effect of mechanical working will be further considered in Chapter X. Meanwhile attention will be confined to the other factors.

In describing the $\gamma \rightarrow \alpha$ transformation in iron it was explained that there is a certain crystallographic relationship between the parent phase

and the precipitated phase, i.e. in this case (111) planes in the γ become (110) planes in the α . Under all conditions this relationship influences the crystallographic orientation of the crystals of the precipitated phase, but it does not always affect their shape or distribution. In all cases of precipitation from solid solution similar conditions are realized. There is a crystallographic relationship between the parent and precipitated phases, and while this always influences the crystallographic orientation of the precipitated phase its effect on the shape of the crystals varies with other factors. The change from γ - to α -iron is a polymorphic change rather than a change in solubility, but when α -iron is being formed from a solution of carbon in γ -iron the process is identical with the changes at present under consideration. This change is described in the next section. Meanwhile, it may be said that at a temperature that decreases as the carbon content increases α -iron begins to precipitate from solid solution and continues to do so as the temperature falls. If the rate of cooling is



FIG. 155. α -Fe (white) forming from austenite (black). $\times 820$.

slow the α -iron crystals begin to form at the boundaries of the solid solution, and from these points irregular rounded crystals like those shown in Fig. 149 develop. When the rate of cooling is increased, α -iron crystals begin to form at points in the interior of the solid solution crystals as well as at the boundaries, and wherever they begin to form, these crystals, instead of growing more or less in all directions as in Fig. 149, tend to grow preferentially in one direction as shown in Figs. 150 and 155. A further increase in the rate of cooling is accompanied by a further increase in the tendency of the crystals of α -iron to form at points within the solid solution crystals and to grow preferentially in certain directions. The subject is fully discussed in Chapter XI in which intermediate conditions between those shown in Fig. 149 and 150 are described. Attention will for the time be confined to the two extreme cases and to the question, how does the rate of cooling alter the distribution of the points at which the formation of α -iron begins and the shape of the crystals that grow from them? This also is fully discussed in Chapter XI, but the following brief account is included here.

The change in orientation at the boundary between one crystal and another is accompanied by some distortion of the lattice. Crystals are therefore less stable at the boundaries than elsewhere, and consequently these are favourable places for new phases to make their appearance. Under equilibrium conditions transformations in the solid almost

invariably begin at the boundaries of existing crystals when these are not too large. Increasing the rate of cooling depresses the beginning of the change, and the further the alloy is cooled before the change begins the more unstable it becomes, i.e. the greater is the tendency to change. Under these conditions the change need not be confined to the boundaries but is able to begin at points within the crystals. In addition to this the growth of precipitated crystals of microscopically visible dimensions involves a certain amount of diffusion, and the requisite amount can take place more easily when a large number of well-distributed crystals exist than when there is a comparatively small number concentrated at certain places. Thus, whereas during slow cooling a change in the solid begins at and extends from the boundaries of the existing crystals, an increase in the rate of cooling tends to promote the appearance of new crystals within them, and when the rate of cooling is sufficiently rapid the new phase begins to precipitate at points more or less equally distributed throughout the whole alloy.

It appears that crystals of a precipitating phase tend to develop in such a way that more or less regular shapes like those shown in Fig. 155 are formed. Surface tension tends, however, to round these off and to produce those shown in Fig. 149. The effect of this depends on the time for which it is allowed to act and on what may be described as the crystallizing power of the crystals concerned. If this is great relative to the surface tension, crystalline shapes will be common; if it is small, as in the case of α -iron, rounded shapes will usually be formed. Diffusion also influences the shape of the crystals of the precipitating phase and it is responsible for the transition from crystals of the type shown in Fig. 149 to those in Fig. 150. When crystals of α -iron grow from a solid solution of carbon in γ -iron, carbon is rejected from the former and diffuses into the remaining γ -iron. From a point on an α -iron crystal carbon can diffuse in all directions into γ -iron. From an edge it can diffuse in all directions perpendicular to the edge, but diffusion from each point on the edge is restricted by the fact that it is also taking place from neighbouring points. From any point on a face, diffusion can only take place at right angles to it, for while the face is advancing, carbon must diffuse away from every point. It will thus be seen that a point on an α -iron crystal can advance more rapidly than an edge and an edge more rapidly than a face. During slow cooling these factors are of little importance for there is plenty of time for the rejected carbon to diffuse into the remaining γ -iron. When the rate of cooling is increased, however, the time required for the diffusion to take place tends to restrict the growth of the α -iron crystals. The advance of the faces is first retarded, and the crystals tend to grow as thin lens-shaped plates, cross-sections of which are shown in Fig. 150. In a direction perpendicular to the plane of the micrograph the dimension of these plates may be equal to the long axis shown there. If, however, the rate of cooling is fast relative to the rate of diffusion of carbon, the points shown in Fig. 150

will tend to become real points instead of cross-sections of sharp edges, i.e. the crystals will tend to become needles rather than plates.

When crystals grow in certain directions in preference to others these correspond to crystallographic directions. Thus, when the crystals of α -iron form plates the planes of these are (110) planes in the crystals. But the (110) planes in the α -iron correspond to (111) planes in the γ -iron, and thus the α -iron plates are parallel to the (111) planes in the γ -iron. Consequently, as a result of the crystallographic relationship between

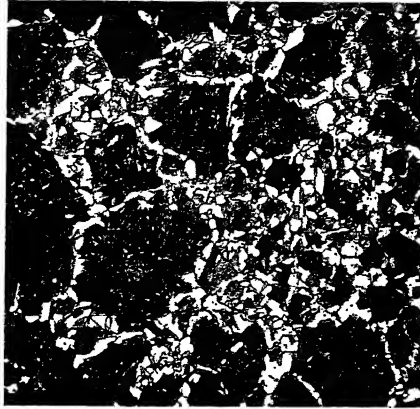


FIG. 156. α -Fe (white) forming from austenite (black). $\times 100$.

the γ - and α -iron the crystallographic planes in the γ -iron influence the directions in which α -iron crystals grow when their growth is confined to certain directions as a result of retarded diffusion.

In all alloys the structures resulting from changes in the solid are affected by the factors described above, but many variations are possible. Some precipitating constituents are less affected by surface tension than others. The range of cooling rates within which the crystals change from the massive (Fig. 149) to the plate form (Fig. 150) varies from alloy to alloy, and in general numerous different distributions and shapes of crystals may be obtained in different alloys cooled at different rates. Even in the case of crystals formed at existing grain boundaries there are possible variations in distribution and shape. In the example illustrated in Fig. 149 comparatively large rounded crystals are formed, and at an earlier stage in their growth they are seen to be definitely isolated from each other. Increasing the rate of cooling or the carbon content of the γ -iron from which these crystals grow causes the formation of chains of smaller crystals as shown in Fig. 156, and a further increase in the carbon content of the austenite results in the formation of definite boundary envelopes like those shown in Fig. 157. In the case of crystals that form plates or needles parallel to the crystallographic planes in the basis solid solution, variations in size, shape, and distribution arise from differences

in the alloys concerned, the rate of cooling and the amount of precipitated phase formed.

The structure formed when a phase is precipitated as plates or needles parallel to crystallographic planes in another phase is known as the Wid-

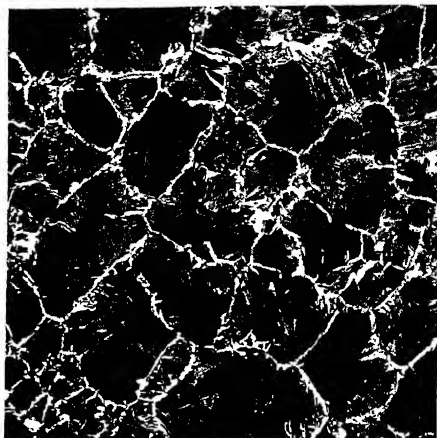


FIG. 157. Boundary films of α -Fe. $\times 100$.

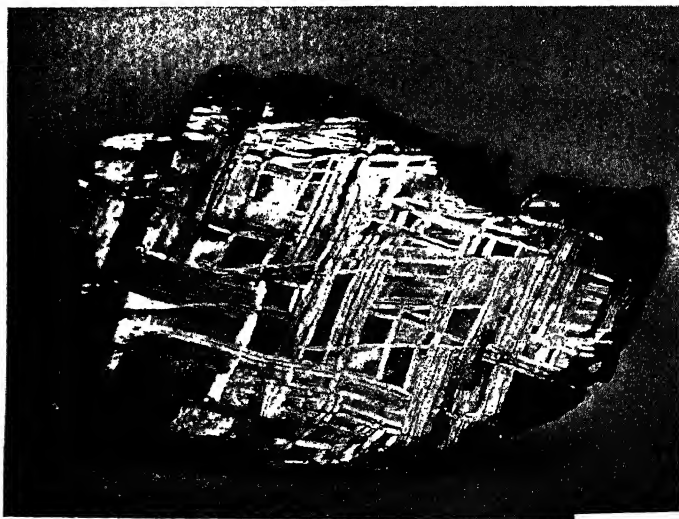


FIG. 158. Structure of meteorite. $\frac{1}{2}$ natural size.

manstätten structure after Alois de Widmanstätten who first observed it in meteorites in 1808. Several examples of this are shown in Figs. 158-66. Fig. 158 is a small portion of a meteorite photographed at half natural size. Meteorites are fragments of planets, and although they are essentially iron-nickel alloys, the slow rate at which they cool in the

planet gives them a structure quite different from that of terrestrial alloys. In these alloys equilibrium conditions are realized, while in terrestrial iron-nickel alloys we deal with persistent rather than stable states. At high temperatures meteorites are face-centred cubic solid solutions of nickel in iron. As they cool an iron-rich body-centred solid solution (kamacite) is precipitated and the nickel content of the remaining face-centred solid solution (taenite) increases. This precipitation takes place along the (111) planes in the face-centred solid solution which become



FIG. 159. The Widmanstätten structure in cast steel. Section parallel to (100) planes in the austenite. $\times 20$ (Belaiew).

the (110) planes in the body-centred solid solution. The mechanism of the change is the same as that of the $\gamma \rightarrow \alpha$ change in iron, and the structure developed consists of plates of kamacite parallel to the (111) planes in the taenite. This sometimes undergoes a eutectoid change and becomes plessite. It is in this respect that meteorites differ constitutionally from terrestrial iron-nickel alloys, but for the present purpose this change may be neglected and Fig. 158 may be said to represent the structure produced when plates of kamacite are formed along the (111) planes in the face-centred solid solution (taenite). The whole area shown in this figure was occupied by one crystal of the face-centred solid solution before the kamacite formed. Thus all the kamacite plates are parallel to (111) planes in one crystal. The geometrical pattern formed by these plates depends on the position of the plane examined relative to the four sets of (111) planes. This is shown clearly in Figs. 159, 160, and 161. These micrographs were taken by Belaiew from a specially prepared cast of 0.55 per cent. carbon steel and they show α -iron plates (white) formed along the (111) planes in the γ -iron (represented by the dark areas). Each micrograph represents a section cut in a given direction relative to the (111) planes in one γ -iron crystal. Thus Fig. 159 shows the pattern when the plane examined is parallel to a (100) plane in the

γ -iron crystal, Fig. 160 shows the pattern when the plane examined is parallel to a (111) plane, and Fig. 161 shows the pattern when the plane examined is parallel to a (110) plane.



FIG. 160. The Widmanstätten structure in cast steel. Section parallel to (111) planes in the austenite. $\times 20$ (Belaiew).

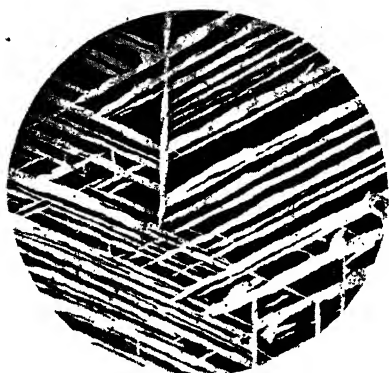


FIG. 161. The Widmanstätten structure in cast steel. Section parallel to (110) planes in the austenite. $\times 20$ (Belaiew).

When γ -iron contains less than 0.9 per cent. of carbon α -iron is precipitated as described, and when it contains more than this amount Fe_3C is deposited. When the rate of cooling is slow and the γ -iron crystals of small or moderate size, the carbide is precipitated in the form of envelopes round the crystal boundaries as shown in Fig. 151. An increase in the rate of cooling or in the size of the γ -iron crystals tends, however, to promote its deposition in their interiors. In this case long plates or needles are formed as shown in Figs. 162 and 163. Although they are

precipitated from γ -iron in a similar manner to the α -iron plates shown in Figs. 159–61, the plates of carbide are not parallel to the (111) planes in γ -iron. The α -iron plates are parallel to the (111) planes in γ because the arrangement of atoms on (111) planes of the face-centred

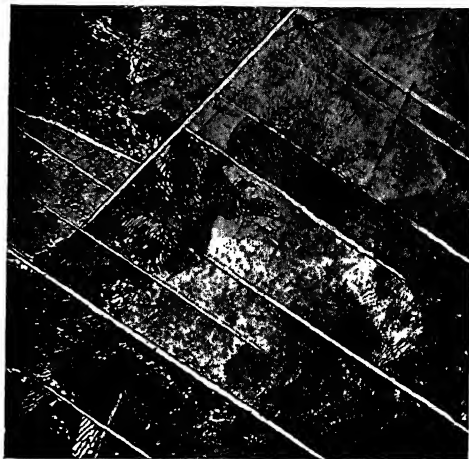


FIG. 162. Plates of Fe_3C . $\times 820$.

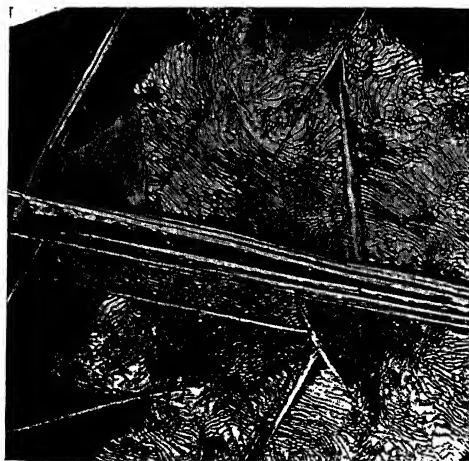


FIG. 163. Plates of Fe_3C . $\times 820$.

lattice is very similar to that on the (110) planes of the body-centred lattice and in consequence these planes become directions of easy growth. Different relations exist, however, between γ -iron and Fe_3C which has an orthorhombic lattice with 12 iron and 4 carbon atoms per unit cell, the dimensions of which are $a = 4.518 \text{ \AA}$, $b = 5.069 \text{ \AA}$, and $c = 6.736 \text{ \AA}$. These relations have been studied by Mehl, Barrett, and Smith (86), who found that the plane of the Fe_3C plates was parallel to

one of the sides of the unit orthorhombic (Fe_3C) cell, but were unable to discover the exact relations between these plates and the γ -iron lattice. Their results indicate, however, that the plane of the carbide plates is parallel to some plane or planes near to (521) and (722) and definitely not parallel to (111).



FIG. 164. 0.1 per cent. C steel, water quenched. $\times 820$.



FIG. 165. 1.7 per cent. C steel, water quenched. $\times 100$.

The other three examples of Widmanstätten structures (Figs. 164-6) are those obtained by the rapid cooling of iron-carbon alloys. These types of structure are fully described in Chapter XI. Fig. 164 illustrates the kind of structure obtained when an alloy containing 0.1 per cent. of carbon is quenched in water from a range of temperature in which it consists of a solid solution of carbon in γ -iron. During the rapid cooling the γ -iron changes to α , but the carbon remains in solution and a solid solution of carbon in α -iron is produced. The structure

illustrated here differs from those previously described in that only one constituent is present, and the Widmanstätten structure arises from the fact that during the change plates of α are formed along the (111) planes in the γ , and although these plates are constitutionally similar, their crystallographic orientation is different and they are thus distinguished. It has already been explained that when the $\gamma \rightarrow \alpha$ change in pure iron is depressed and accelerated by rapid cooling, the α -iron forms plates along the (111) planes in the γ . Thus by water quenching iron of high purity, structures similar to that shown in Fig. 164 have



Fig. 166. 0.75 per cent. C steel quenched in molten lead. $\times 820$.

been obtained by Mehl and Smith (87) and Sauveur and Chou (88). In the iron used by the former the total percentage of impurities was 0.038. Fig. 165 illustrates the type of structure obtained when a steel containing 1.7 per cent. of carbon is quenched in water from a range of temperature in which it consists entirely of a solid solution of carbon in γ -iron. In this case only a portion of the γ -iron changes to α during cooling, and thus the resulting structure consists of plates of α -solid solution (dark) in a matrix of γ -solid solution (light). Fig. 166 shows the structure obtained when a steel containing 0.75 per cent. of carbon is quenched in molten lead at 385° C. and retained at this temperature until the γ -solid solution has partly decomposed.

Mehl and his co-workers Barrett, Rhines, Marzke, and Smith, and several other workers including Belaiew, Young, Phillips, Kurdjumow, and Sachs have made careful studies of the Widmanstätten structure in different alloys in order to discover the relations between the basis solid solutions and the precipitated constituents. The results obtained up to 1932 are tabulated by Mathewson and Smith (89) but several investigations have since been published. In general it has been possible to ascertain (1) the planes in the basis solid solution along which plates of the precipitated phase are formed, and (2) the crystallographic plane in the precipitated phase that is parallel to the plane of the plates. Thus just as it is known (1) that plates of α -iron form

along (111) planes in γ -iron, and (2) that the (110) planes in the α -iron are parallel to the plane of these plates, so similar relations have been established for other changes. Furthermore, just as it is known that the relations between α -iron plates and γ -iron crystals arise from the fact that the rearrangement of atoms on the (111) planes of the face-centred lattice permits an easy transition to (110) planes in the body-centred lattice, so it may be inferred that similar conditions arise in other changes. In concluding this section some of these other changes may be described.

Mehl, Barrett, and Rhines (90) obtained Widmanstätten structures in aluminium-copper alloys containing between 1 and 5 per cent. of copper by water-quenching from 540°C . so as to retain all the copper in solid solution and heating for two weeks at $250\text{--}300^{\circ}\text{C}$. to allow CuAl_2 to precipitate. The compound was found to form short plates parallel to the (100) planes in the solid solution matrix, but during the prolonged heating many of them were converted into globules by the action of surface tension. This is a change that is very closely associated with precipitation, for constituents that come out of solution in the form of plates are always liable to globularize if heated at a high enough temperature or for a long enough time. Definite results were not obtained in connexion with a study of the relations between the orientation of the CuAl_2 and the plane of the plates. The evidence indicated, however, that the base of the unit tetragonal cell of CuAl_2 was parallel to the plane of the plates and therefore to the (100) planes in the solid solution. In a similar system, viz. the aluminium- Mg_2Si system, the same investigators found that Mg_2Si was precipitated under suitable conditions as plates parallel to the (100) and (110) planes in the face-centred solid solution matrix. The relations between the orientation of the Mg_2Si and the solid solution were not determined. In another similar system, namely, aluminium-silver, Mehl and Barrett (91) found that the silver rich constituent γ which is precipitated from solid solution in aluminium forms plates parallel to the (111) planes in the aluminium. This γ -constituent has a close packed hexagonal lattice and the basal plane of the unit hexagonal cells was found to be parallel to the plane of the plates, and thus to the (111) planes in the solid solution matrix.

Silicon is soluble in copper to the extent of 6.7 per cent. at 750°C ., and 4 per cent. at 300°C . During cooling from 750°C . to 300°C . silicon is therefore precipitated from solid solution and a silicon-rich constituent known as γ is formed. Mehl and Barrett (91) tried to obtain Widmanstätten structures in these alloys by controlled rates of cooling, but found it necessary, as in the other alloys mentioned above, to resort to quenching to retain the silicon in solution followed by heating to 350°C . to allow γ to precipitate. They were unable to determine the planes on which the γ -plates were formed, but established that they were not (111) but must be some planes of which there are 12 sets.

Besides the examples described in this section a number of other alloys in which Widmanstätten structures are developed have been studied. Some of these will be described later in connexion with the structures produced when one constituent changes to another. Enough has been said to show (1) that constituents formed as a result of changes in solid solubility are crystallographically related to the solid solution from which they form, (2) that under certain conditions these constituents form plates parallel to crystallographic planes in the solid solution, and (3) that the crystallographic planes on which these plates are formed are determined by the crystallographic relations between the constituents concerned and not by the crystal structure of the solid solution only. Thus while the basis solid solution in all the examples described is face-centred cubic, α -iron and γ -Al-Ag form along (111) planes, CuAl_2 forms along (100) planes, Mg_2Si forms along (100) and (110) planes, and Fe_3C and γ -Cu-Si form along planes of high index.

CHANGES FROM ONE CONSTITUENT TO ANOTHER

Changes of the type now under consideration occur in systems of Types 3A, 3C, 3D, 4, 5, and 6. In general they are associated with polymorphic transformations or with alterations in the range of stability of solid solutions or intermediate constituents. Systems of Types 3C and 3D differ from those of Type 2 by reason of the polymorphic changes that occur in one or both of the component metals. In these systems, and also in those of Types 3A, 4, and 6, the formation of one solid constituent from another is associated with a polymorphic change, and it is only in systems of Type 5 that changes of this kind are associated with alterations in the range of stability of solid solutions or intermediate constituents. It should be stated again, however, that when some of the systems of Type 4 are considered as a whole they are similar to those of Type 5 and the classification adopted in Table 24 is obtained by taking account of the useful range only.

The formation of one constituent from another involves solid diffusion and a change in space lattice. A transformation of this kind therefore bears a close resemblance to a change in solid solubility, and for this reason the formation of α -iron from a solid solution of carbon in γ -iron was used in the last section to illustrate the kind of structures formed when a constituent is precipitated from a solid solution. An example of a change from one constituent to another is shown in Fig. 119, and in order to describe the transformation part of this diagram is reproduced in Fig. 167. As explained in Chapter V, iron-nickel alloys containing less than 3.2 per cent. of nickel solidify as solid solutions of nickel in δ -iron (i.e. the body-centred form stable above 1,403° C.). Alloys containing more than 4.3 per cent. of nickel consist when completely solid of a solid solution of nickel in γ -iron (i.e. the face-centred form stable between 1,403° C. and 906° C.). Alloys containing between 3.2 and

4.3 per cent. of nickel consist when solid of two solid solutions, namely, δ of composition c and γ of composition d . The face-centred γ solid solution appears in alloys containing more than 3.2 per cent. of nickel because this metal raises the temperature of the $\delta \rightleftharpoons \gamma$ change until it meets the solidus, and the raising of this transformation is represented by the two lines hc and hd (Fig. 167). Pure iron is in the δ -form above h and in the γ -form below it. Iron-nickel alloys are in the δ -form above

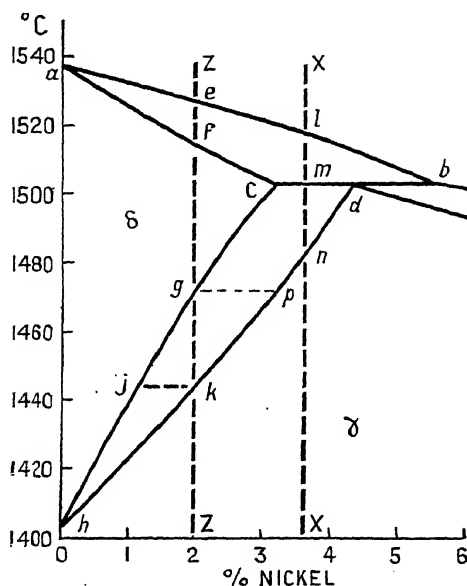


FIG. 167. Iron-nickel alloys.

hc and in the γ -form below hd . Thus in alloys the $\delta \rightleftharpoons \gamma$ change is spread over a range of temperature and the lines hc and hd have the same significance as the liquidus and solidus lines in Figs. 113, 114, 115, &c.

In the alloy Z solidification begins at the point e and is completed at point f , when the alloy consists under equilibrium conditions of a homogeneous body-centred cubic solid solution of composition Z . No change takes place in the solid solution until it is cooled to g when a face-centred solid solution (γ) begins to form from δ in the same way as a primary solid solution forms from a melt. The γ solid solution first formed is of composition p , and as this contains more nickel than the δ from which it is formed the nickel content of the remaining δ is diminished. Thus as the temperature falls, γ of progressively varying composition is formed along the line pk and the remaining δ changes in composition along gj . Under equilibrium conditions the two solid solutions remain homogeneous throughout the change, i.e. at any temperature the composition of the δ as a whole is represented by a point on gj and that of the γ by a

point on pk . At the temperature of the line jk the transformation is complete, for then the γ is of the same composition as the alloy.

The change described above involves a transformation from one solid solution to another and is very similar to a change from a liquid solution to a solid solution. All that was said in Chapter V about the solidification of primary solid solutions applies to the change under consideration. Thus the γ solid solution is formed from the δ by a process of 'selective crystallization' which is similar to selective freezing, the formation of γ by this process is accompanied by diffusion in the γ and in the δ , and under equilibrium conditions this keeps the two solid solutions homogeneous. As, however, diffusion in the γ tends to bring it to an average composition different from that represented by the appropriate point on hk , there is also diffusion of iron from δ to γ . Furthermore, the formation of γ by selective crystallization is not affected by time to the same extent as the processes of solid diffusion. Thus the condition of the alloy at the completion of the change depends on the rate of cooling through the range of transformation. Increasing the rate of cooling lowers the beginning of the change and causes it to be spread over a wider temperature interval. Solid diffusion does not keep pace with selective crystallization, and consequently the γ produced is not homogeneous. When the rate of cooling exceeds that required for equilibrium, three lines like BK , BV , and BP in Fig. 112 are required to represent the conditions in the γ . dh (Fig. 167) is the equivalent of BK (Fig. 112) but for each alloy and each rate of cooling lines equivalent to BV and BP must be drawn. As the rate of cooling is increased these lines swing farther away from dh , as it is decreased they swing towards it and coincide with it for an equilibrium rate of cooling.

In one important respect, however, the change under consideration differs from the solidification of a primary solid solution, viz. the liquid in the latter case is replaced by a solid solution in the former. Thus while it was possible to assume, in describing the solidification of solid solutions, that diffusion in the liquid kept pace with the formation of solid, this assumption cannot be made in the present case, and the effect of restricted diffusion in the δ has to be taken into account. This phenomenon will be considered presently.

The alloy X in Fig. 167 consists of two solid solutions when completely solidified at the point m . Its condition at solidification is similar to that of the alloy Z at an intermediate stage in the solid transformation—say at $1,460^\circ\text{C}$. As it cools from m selective crystallization and solid diffusion proceed, the amount of γ increases at the expense of δ , the δ changes in composition along ch and the γ along dh . At n the transformation is complete. All alloys between c and d behave in the same way as X and all to the left of c behave in the same way as Z .

Carbon, like nickel, raises the $\delta \rightleftharpoons \gamma$ transformation in iron and the solidification of alloys containing less than 1.7 per cent. of carbon is similar to that of iron-nickel alloys, i.e. by altering the compositions

and temperatures represented by the various points Fig. 119 may be made to represent the solidification of iron-carbon alloys containing up to 1.7 per cent. of carbon. Beyond this amount the iron-carbon diagram is quite different, for 1.7 per cent. is the limit of solid solubility of carbon in iron. Carbon, like nickel, also lowers the $\gamma \rightleftharpoons \alpha$ change, and as it is with this that we are now concerned we may say that at 1,130° C. all iron-carbon alloys up to 1.7 per cent. carbon are solid solutions of carbon in γ -iron. Below this temperature two changes occur, viz. the

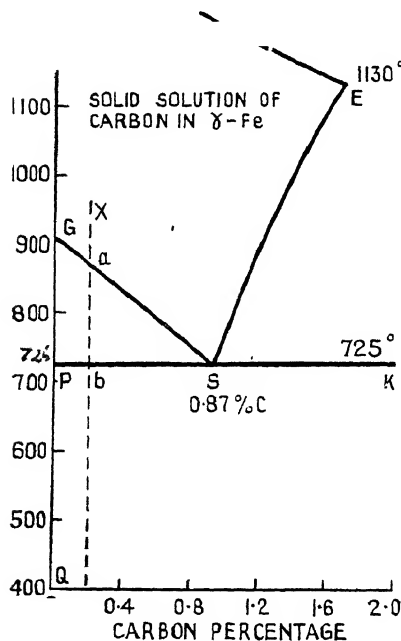


FIG. 168.

solubility of carbon in γ -iron decreases and the iron transforms from γ to α . These changes are represented in Fig. 168. The line *ES* in this figure has the same significance as *bd* in Fig. 153, i.e. it represents a decrease in solid solubility with falling temperature. If the iron remained in the γ form down to atmospheric temperature, this line would continue below *S* and the iron end of the iron-carbon diagram would be the same as the aluminium end of the aluminium-copper system (Fig. 153). The difference, represented by the lines *GS* and *PSK*, arises from the fact that γ -iron changes to α which does not dissolve appreciable amounts of carbon.

An alloy containing 1.7 per cent. of carbon solidifies as a solid solution of carbon in γ -iron. Solidification is complete at 1,130° C. As

soon as the alloy is cooled below this temperature the solid solution becomes supersaturated with carbon and this begins to be precipitated as Fe_3C . As the temperature falls this continues to form while the solid solution changes in composition along *ES*. The iron carbide forms a network round the crystals of solid solution as shown in Fig. 151 or plate-like crystals as shown in Figs. 162 and 163. At 725° C. only 0.87 per cent. of carbon remains in solid solution in the γ -iron. In alloys containing between 0.87 and 1.7 per cent. of carbon the formation of Fe_3C does not begin until they are cooled to a temperature below 1,130° C., viz. to the appropriate point on *SE*. It then proceeds as above.

Pure iron changes from γ to α at 906° C. When carbon is dissolved in the γ -iron the temperature at which this change begins is depressed and the line *GS* (Fig. 168) represents the lowering of the $\gamma \rightarrow \alpha$ change

with increase in carbon content. In other words, this line shows the temperature at which the $\gamma \rightarrow \alpha$ change begins in alloys of different carbon content. The alloy X is a solid solution of carbon in γ -iron above the point α . When it is cooled to this point α -iron begins to form. This contains practically no carbon, and the carbon dissolved in the areas where it is formed is driven into the remaining γ -iron. This increases the carbon content of the γ -iron and no more α is formed until the temperature falls. The conditions are the same as those described in Chapter V in connexion with the solidification of an alloy on the zinc side of the Zn-Sn eutectic. As the temperature falls α -iron continues to form and crystals like those shown in Fig. 149 are produced, while the γ solid solution changes in composition along GS . At 725°C . the γ -iron contains 0.87 per cent. of dissolved carbon and the amount of γ solid solution is to the amount of α as Pb is to Sb. A similar change occurs in all alloys containing less than 0.87 per cent. of carbon. When they are cooled to the appropriate point on GS , α -iron begins to deposit and continues as the temperature falls, while the composition of γ solid solution changes along GS .

Fig. 168 is clearly similar to Fig. 108 (i.e. the Sn-Zn system) except that there is a solid solution instead of a melt and the composition of the phase separating along SE is not represented by a vertical line at 1.7 per cent. carbon. (Fe_3C actually contains 6.66 per cent. carbon.) Otherwise the conditions are similar. Fe_3C separates from solid solution along ES just as tin is deposited from the melt along CE , and α -iron is formed along GS just as zinc is formed along AE . Furthermore, S (Fig. 168) is common to GS and ES just as E (Fig. 108) is common to AE and CE . At S α -iron and Fe_3C are formed simultaneously from γ solid solution containing 0.87 per cent. carbon in the same way as tin and zinc are formed simultaneously from a melt containing 92.1 per cent. tin. Point S resembles a eutectic point except that the two constituents produced are formed from a solid solution instead of a liquid solution. To indicate this similarity without ignoring the difference S is called a eutectoid point. Just above it, γ -iron containing 0.87 per cent. of carbon in solution is stable, because at 725°C . it can dissolve this amount and because this stabilizes γ -iron down to 725°C . Just below it, γ -iron containing 0.87 per cent. carbon is unstable, for less than this amount is soluble and more than this amount would be required to stabilize the γ -iron. Thus, on cooling from just above S to just below it, Fe_3C and α -iron are formed simultaneously and the γ solid solution disappears. In all alloys the transformation of the γ solid solution is completed at S and the line PSK is drawn right across the diagram to show this.

The formation of Fe_3C along the line SE is similar to the other changes described in the previous section, and the eutectoid change at S will be further considered in the next section. Meanwhile attention may be confined to the formation of α -iron. This has been described above as if

the α -iron contained absolutely no carbon. Actually, however, 0.035 per cent. of carbon is soluble in α -iron at P and about 0.007 per cent. is soluble at Q . The diagram should therefore contain a line GPQ corresponding to abd in Fig. 153. The lines GS and GP then have the same significance as the liquidus and solidus lines in Figs. 113, 114, 115, &c., or as the lines ch and dh in Fig. 167. The extent of the solubility of carbon in α -iron is too small, however, to show to scale in Fig. 168, and although it has an important bearing on certain phenomena exhibited by steel it may for the time being be neglected. When this is done the formation of α -iron from γ -iron becomes a convenient transformation for illustrating the effect of restricted diffusion in the solid solution that takes the place of the liquid.

GS (Fig. 168) has the same significance as a liquidus line in any of the systems described in Chapter V, e.g., Figs. 107, 115, 119, &c. In describing these lines it was stated that a liquidus represents (1) the composition of the liquid that can exist in equilibrium with a corresponding solid at a given temperature, (2) the change in the composition of the liquid during the solidification of a given alloy, and (3) the temperature at which the solidification of any alloy begins. In the same way GS (Fig. 168) represents (1) the composition of γ solid solution that can exist in equilibrium with α -iron at a given temperature, (2) the change in the composition of the γ solid solution during the formation of α -iron in a given alloy, and (3) the temperature at which the formation of α -iron begins in alloys containing less than 0.87 per cent. carbon. It was further stated in Chapter V that the significance of the liquidus does not alter much with variations in the rate of cooling except that under-cooling prevents solidification beginning as soon as the appropriate point is reached. The significance of the solidus was shown on the other hand to vary greatly with the rate of cooling. Although GS has the same significance as a liquidus it applies to changes in a solid and is thus affected by the rate of cooling in the same way as a solidus.

Under equilibrium conditions of cooling the line GS has the full significance mentioned above. When the rate of cooling is faster than this the line has little to do with the changes that occur, except that at a given temperature γ solid solution containing more carbon than is represented by the appropriate point on GS cannot be formed. Even in pure iron the $\gamma \rightarrow \alpha$ change may be lowered by increasing the rate of cooling, and the lowering effected by a given increase in the rate of cooling increases with the carbon content. Thus, unless the rate of cooling is very slow, the formation of α -iron does not begin at the appropriate point on line GS . The more the rate of cooling is increased the farther is the beginning of the change lowered, but the actual effects of rapid cooling are complicated by a change in the position of the eutectoid point and finally by the transformation from $\gamma \rightarrow \alpha$ -iron taking place without diffusion of carbon or formation of Fe_3C . These complicated changes are described in Chapter XI. Meanwhile, in order to illustrate the effect

of diffusion of carbon in γ -iron, attention may be confined to rates of cooling that modify without entirely transforming the conditions represented in Fig. 168.

The line GS is shown again in Fig. 169. When alloy X (0.2 per cent. C) is cooled at a rate exceeding the equilibrium rate, α -iron does not begin to form at the appropriate point on GS but at some lower temperature such as a . This is a point on the line that represents the temperatures at which the change begins in alloys of different composition cooled at this particular rate, but this line need not be drawn because it has no further connexion with the course of the change in alloy X . Immediately the formation of α -iron begins at a the carbon content of the γ solid solution in contact with α -iron is increased to b on the line GS . It cannot be increased beyond this for GS represents the highest carbon content of γ -iron in contact with α -iron at a given temperature. As the temperature falls from T_1 to T_2 α -iron continues to form and the carbon content of the γ -iron in immediate contact with it is increased to c . The formation of an infinitely small amount of α -iron is, however, sufficient to raise the carbon content of the γ -iron in immediate contact with it from a to c if this carbon does not diffuse into the remainder of the γ -iron. The amount of α -iron formed depends on the amount of carbon transferred to the γ -iron, i.e. on the extent to which the average carbon content of the γ -iron is increased. If the time taken to cool from T_1 to T_2 does not permit the carbon rejected by the α -iron to diffuse uniformly throughout the γ , then at T_2 the carbon content of the γ -iron remote from α -iron will be less than c . If the carbon content of this γ -iron is d then the average carbon content will be, say, e . If this rate of cooling is continued the carbon content of the γ -iron in contact with α -iron will alter along bcs , that of the γ -iron remote from α -iron along adf , and the average carbon content will alter along aeg . At any temperature there will be a concentration gradient in the γ -iron and the amount of α -iron formed will be less than under equilibrium conditions. Thus at T_2 the amount of α is to the amount of γ as jl is to hj under equilibrium conditions and as jk is to hj under the conditions of more rapid cooling in question.

The completion of the transformation during rapid cooling is described in Chapter XI. Attention may for the time be confined to the

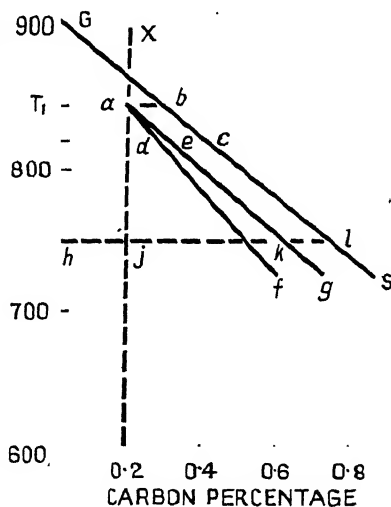


FIG. 169.

effect of the concentration gradient established in the γ -iron. Under the conditions illustrated in Fig. 169 the temperature and composition of the major portion of the γ solid solution is represented by points below *GS*. The only portion that is really stable is that in immediate contact with α -iron. This condition arises because time is not available for carbon to diffuse uniformly throughout the γ -iron. But there is no reason why the formation of α -iron should take place entirely by the growth of the crystals originally formed at *a*. At all stages in the transformation most of the γ -iron contains less carbon than is required to stabilize it and more α -crystals may therefore appear. The effect of their formation depends on the rapidity of their appearance. If, e.g., new α -crystals were to appear with great rapidity throughout the γ , then a system of such minute crystals would be formed that the distances over which carbon had to diffuse would be negligibly small and pronounced concentration gradients would not result. Actually, however, new α -crystals are formed comparatively slowly, and existing crystals in contact with γ -iron containing the amount of carbon indicated by the line *GS* continue to grow without large numbers of new crystals appearing in regions where the carbon content is less. Thus, although the formation of new α -crystals increases the number present and has a quantitative effect on the transformation, it does not alter the general significance of Fig. 169.

In general, when the rate of cooling is faster than the equilibrium rate the beginning of the transformation is depressed, the carbon rejected by the α does not diffuse uniformly throughout the γ , and the amount of α formed in a given temperature range is decreased. As the rate of cooling is progressively increased beyond the equilibrium rate the above effects become increasingly pronounced. They are counterbalanced to some extent by the formation of increasing numbers of new crystals, but despite this the general conditions illustrated by Fig. 169 are not altered. In all changes in the solid similar conditions are realized, but their effect depends on the nature of the change and the temperature at which it takes place. In iron-carbon alloys containing less than 0.18 per cent. of carbon a transformation from δ to γ solid solution takes place above 1,400° C. by a process of selective crystallization similar to that illustrated in Fig. 167. At this temperature, however, the rate of diffusion of carbon in solid iron is very rapid and no pronounced concentration gradients are produced in either phase. The diffusion of nickel in iron is less rapid, and when a particular alloy such as *Z* (Fig. 167) is transforming from δ to γ , lines such as those shown in Fig. 169 are required to represent the conditions in the δ , while lines similar to those shown in Fig. 112 are required to represent the conditions in the γ . As the transformation is completed above 1,400° C. there is, however, ample opportunity for homogeneous crystals of γ to be produced during subsequent cooling. During changes in solid solubility, concentration gradients like those described above are again produced when exact equilibrium is not realized. Thus when CuAl_2 is forming from a solid

solution of copper in aluminium the copper content of the solid solution in immediate contact with CuAl_2 is less than at points more remote, and the concentration gradient thus produced increases with the rate of cooling. Similarly, when Fe_3C is forming from a solid solution of carbon in γ -iron the carbon content of the γ -iron in contact with Fe_3C is less than at points more remote. In other words the conditions realized during cooling are the reverse of those realized during heating and illustrated in Fig. 154.

Another type of change from one constituent to another is represented by the broken loop at the left-hand side of the iron-phosphorus system (Fig. 128) and in order to describe this transformation the loop is shown on an enlarged scale in Fig. 170. This loop arises from the fact that phosphorus depresses the $\delta \rightleftharpoons \gamma$ change and raises the $\gamma \rightleftharpoons \alpha$ change. In pure iron the $\delta \rightleftharpoons \gamma$ change takes place at $1,403^\circ\text{C}$. (point *a*). It is lowered by the addition of phosphorus, and as this change takes place over a range of temperature in alloys, the lines *ab* and *ac* represent this lowering. Similarly, the lines *dc* and *db* represent the raising of the $\gamma \rightleftharpoons \alpha$ change. At 0.55 per cent. of phosphorus and $1,050^\circ\text{C}$. the two changes meet, no γ -iron is formed, and as δ and α are indistinguishable no change occurs. Alloys containing more than 0.55 per cent. phosphorus (e.g. *X*) solidify as δ - (or α -) iron and remain unchanged down to atmospheric temperature. Alloys containing less than 0.50 per cent. (e.g. *Z*) solidify as δ -iron, then change to γ and finally to α , while alloys containing between 0.50 and 0.55 per cent. of phosphorus (e.g. *Y*) solidify as δ , change partially to γ , and then revert to α (or δ) again. Line *ab* is the 'liquidus' for the $\delta \rightarrow \gamma$ change and line *ac* the 'solidus'. Line *cd* is the 'liquidus' for the $\gamma \rightarrow \alpha$ change and line *bd* the 'solidus'.

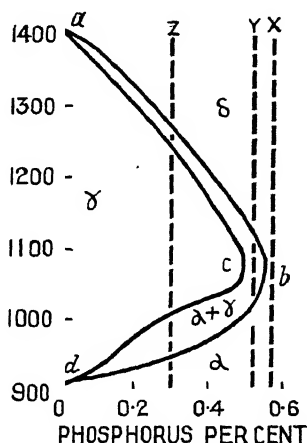


FIG. 170.

Alloy *Y* consists entirely of δ down to $1,125^\circ\text{C}$. when it begins to change to γ . This change is not completed, however, and at a lower temperature the γ formed changes back to α . Alloy *Z* begins to change to γ at $1,270^\circ\text{C}$. and under equilibrium conditions this change is completed at $1,240^\circ$. As cooling continues no change takes place until $1,020^\circ$ when the reverse change $\gamma \rightarrow \alpha$ begins and is completed at 945°C . As the rate of diffusion of phosphorus in iron is slow, heterogeneity is liable to result from the selective crystallization that accompanies these changes, and this applies more particularly to the $\gamma \rightarrow \alpha$ change which in most alloys takes place at a much lower temperature than the $\delta \rightarrow \gamma$ change. Loops similar to that shown in Fig. 170 occur in the diagrams

for the alloys of iron with chromium, silicon, tungsten, molybdenum, vanadium, and aluminium.

As a final example of the formation of one constituent from another the changes in solid copper-zinc alloys may be described. Part of the diagram for these is given in Fig. 129 and reference to this will show that the composition ranges of stability of the constituents alter with temperature. Alloys that lie to the left of b (32.8 per cent. Zn) solidify as α and undergo no changes during subsequent cooling. Alloys that lie between b and c (i.e. 32.8 and 37 per cent. Zn) solidify as mixtures of two solid solutions namely, α of composition b and β of composition c . As these alloys cool, the composition of the α changes along the line bn and that of the β along the line cm . At the same time the amount of α increases at the expense of β . When the vertical representing the composition of an alloy crosses the line bn , all the β has been transformed to α . Thus, as alloy X cools from 905° C. to 800° C. the amount of α increases at the expense of β and below 800° C. it consists entirely of α . Alloys between c and e solidify as β , but the range of stability of this constituent decreases as the temperature falls. If the vertical line representing the composition of an alloy meets cm , then α begins to form from β . This change begins in alloy Y at about 825° C. and as the temperature continues to fall the amount of α continues to increase. At 700° C. alloy Y consists of β of composition m and α of composition n . If the line representing the composition of an alloy meets el , γ begins to form from the β . This occurs in alloy Z at 800° C. and at 700° C. it consists of β of composition l and γ of composition k . Alloys that lie between e and f (i.e. 56.4 and 61 per cent. Zn) solidify as mixtures of β of composition e and γ of composition f . In those containing between 60 and 61 per cent. of zinc the β changes to γ when the line fk is crossed. The remainder of these alloys undergo no change.

The composition ranges of stability at solidification and room temperature respectively are shown in Fig. 171. As α is stable up to 38.1 per cent. Zn at atmospheric temperature, the alloys between 32.8 and 37 per cent. Zn that solidify as $\alpha+\beta$ consist entirely of α at atmospheric temperature. Furthermore, alloys that contain between 37 and 38.1 per cent. Zn solidify as β , then change to $\alpha+\beta$ and finally to α . Thus alloys that consist of α at room temperature may have solidified as α , $\alpha+\beta$, or as β . Alloys that contain between 38.1 and 46.2 per cent. Zn solidify as β but later change partly to α , those that contain between 46.2 and 49.5 per cent. Zn solidify as β and remain unchanged, while those that contain between 49.5 and 56.4 per cent. Zn solidify as β and later change partly to γ .

The structures produced by changes of the type described in this section are controlled by the same factors as those described in the previous section. The two sorts of changes are in fact essentially similar although they are represented in different ways in the diagram. Thus the formation of α -iron from a solid solution of carbon in γ -iron

was used in the previous section to illustrate the kind of structures that result from changes in solid solubility, and the same transformation might be used to illustrate the general features of the formation of γ from δ in the iron-nickel or iron-carbon system or of γ from δ or α from γ in the iron-phosphorus system. The formation of α or γ from β in the

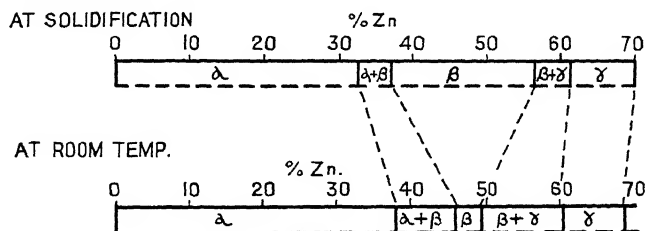


FIG. 171. Illustrating the relation between the composition limits of the constituents at solidification and room temperature in copper-zinc alloys.

copper-zinc and other similar systems is again controlled by the same general laws described in the previous section, but owing to different relations between the factors concerned, different structures result, and these will now be described.

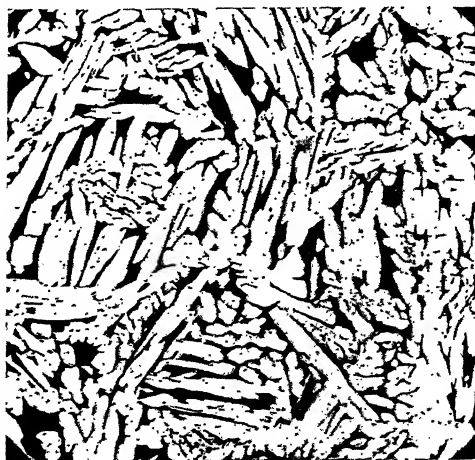


FIG. 172. α and β in Cu-Zn. $\times 100$.

The structure obtained when a copper-zinc alloy that solidifies as β changes partly to α is shown in Fig. 172. The light constituent is the α - and the dark the β -matrix. β has a body-centred and α a face-centred cubic lattice. Thus the lattice change involved is the reverse of that which occurs when γ -iron changes to α , and the relations between the crystal structures determine the type of structure produced. According to Mehl and Marzke (92) the precipitated α takes the form of true needles, but in a later paper Marzke (93) states that plates are formed

when precipitation occurs at low and needles when it occurs at high temperatures. In any case the orientation of the α is related to that of the β in such a way that a (110) plane in the β becomes a (111) plane in the α . The α -plates are parallel to (110) planes in the β and the long axes of the needles are parallel to [111] directions which lie in (110) planes. In alloys that contain between 49.5 and 56.4 per cent. Zn, γ is formed from β during subsequent cooling. This γ is one of the intermediate constituents that have different crystal structures, different properties, and form different kinds of crystals from pure metals and solid solutions. To some extent γ formed from β tends to appear at the boundaries of the β grains, but a characteristic feature of the change is the formation of stars and polyhedrons within the β -grains. According to Mehl and Marzke water quenching prevents the formation of the γ -phase, air cooling permits the formation of small stars, and furnace cooling that of large stars (Fig. 515, Chapter XV). When a quenched specimen is reheated very small stars are first produced, but on prolonged heating polyhedrons like those shown in Fig. 516, Chapter XV, are formed. The relations between the orientation of the γ - and β -crystals have not been established, but it has been shown that the γ -polyhedrons are enclosed by (110) planes of β and that the intersecting planes forming the stars are likewise (110) planes in the β . Thus, although the strong crystallizing power of γ permits it to form crystals that are neither boundary envelopes, plates, or needles, nevertheless the crystallographic relations between the β and the γ control the outward form of the polyhedrons and the directions of the points of the stars.

In copper-aluminium and copper-tin alloys within certain limits of composition α is precipitated from β in the same way as in the copper-zinc alloys. Structures similar to that shown in Fig. 172 are produced, and as the same lattice change (body-centred to face-centred) is involved, (110) planes in the β become (111) planes in the α . According to Mehl and Marzke the α in copper-aluminium alloys forms needles and not plates and the long axes of these needles are parallel to [111] directions in the β . Smith (94) reached the same conclusion with regard to copper-tin alloys, and also to silver-zinc alloys, which form a system similar to those of the copper-base alloys described above.

EUTECTOID CHANGES

A eutectoid change occurs when two constituents are formed simultaneously from a solid solution or an intermediate constituent. The most important change of this kind is that which occurs in iron-carbon alloys when γ solid solution containing 0.87 per cent. of carbon transforms at 725° C. into α -iron and Fe_3C . Owing to its bearing on industrial practice this change has been extensively studied. In copper-aluminium alloys a eutectoid occurs at 570° C., and β containing 11.9 per cent. of

aluminium transforms to α and δ . This also occurs in alloys of industrial importance and has therefore received a certain amount of attention, and the same is the case with the eutectoid in copper-tin alloys which occurs at 520° C. and results in the transformation of β containing 27 per cent. Sn into α and δ . Other eutectoid changes that take place in important alloys of the common metals are as follows: Fe-Al at 43 per cent. Al and 1,100° C., Fe-Cu at 5.5 per cent. Cu and 810° C., Fe-Mo at 63 per cent. Mo and 1,180° C., Fe-N at 1.5 per cent. N and 590° C., Cu-Si at 7.75 per cent. Si and 782° C., Cu-Zn at 74 per cent. Zn and 555° C., Sn-Bi at 2 per cent. Bi and 95° C., Sn-Cd at 4 per cent. Cd and 127° C., and Al-Zn at 79 per cent. Zn and 256° C. None of these, except that in the Al-Zn alloys, are important in connexion with the properties, treatment, or uses of industrially important alloys, and the same may in general be said about the eutectoids that occur in alloy systems that do not come within the scope of this book.

The simultaneous crystallization of two constituents from a solid solution or intermediate constituent usually results in a structure consisting of alternating plates or lamellae of the new phases. This is the typical eutectoid structure, and in alloys in which it is formed it is recognized as a distinct constituent in the same way as a eutectic is. The eutectoid structure formed in iron-carbon alloys from the decomposition of γ solid solution is known as 'pearlite', a micrograph of which is shown in Fig. 134. It consists of alternate lamellae of α -iron and Fe_3C and in each 'grain' of pearlite these lamellae are parallel. In a given specimen the apparent thickness of the lamellae in different grains varies according to the relation between the plane examined and the plane of the plates. If the plane examined cuts the plates in the grain at right angles their true thickness is observed, but as the angle between them and the plane examined decreases the apparent thickness increases. For this reason, in the various grains shown in Fig. 134 the apparent thickness of the plates is different.

An iron-carbon alloy containing 0.87 per cent. of carbon remains a solid solution of carbon in γ -iron until it is cooled to 725° C. Actually it does not begin to change until cooled about 15° C. below this, for whereas 725° C. is the equilibrium temperature of the transformation, it takes place below this during cooling and above it during heating even when the rates of heating and cooling are very slow. Furthermore, the change does not in practice take place at a given temperature but over a range. For the present purpose, however, these qualifications may be ignored and the γ solid solution supposed to transform to pearlite when cooled from just above to just below 725° C. If the alloy contains less than 0.87 per cent. of carbon the formation of pearlite is preceded by the formation of α -iron; if more it is preceded by the formation of Fe_3C . Thus, while an alloy containing 0.87 per cent. of carbon consists entirely of pearlite at temperatures below 725° C., those containing less than this consist of pearlite plus α -iron and those containing more

consist of pearlite plus Fe_3C . As the carbon content decreases from 0.87 to 0 per cent., the amount of pearlite decreases from 100 to 0 per cent. and the amount of α -iron increases from 0 to 100 per cent. As the carbon content increases from 0.87 per cent. to 1.7 per cent. the amount of pearlite decreases from 100 to 86 per cent. while the amount of Fe_3C increases from 0 to 14 per cent.

In the iron-carbon system there is little change in the composition of the α -iron as the temperature of its formation falls, and no change in the

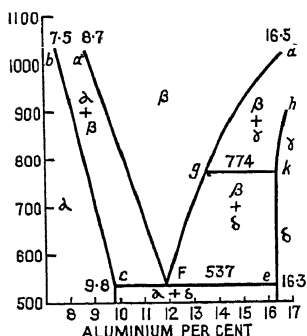


FIG. 173. The eutectoid region in the copper-aluminium system.

composition of the Fe_3C . The conditions are different in the copper-aluminium system the relevant portion of which is shown in Fig. 173. In this figure the eutectoid temperature is given as 537°C . and this value may be used in the following discussion. Actually, however, the accepted value of the eutectoid temperature has been changed from 537° to 570°C . as a result of recent work described in Chapter XV, and in Fig. 519 the eutectoid horizontal is drawn at 570°C . In other respects Figs. 173 and 519 are similar. Alloys containing between 8.7 and 16.5 per cent. of aluminium solidify as β . The alloy of eutectoid composition (viz. 11.9 per cent. Al) undergoes no change until it reaches point F at 537°C . Then the β transforms to a eutectoid of α containing 9.8 per cent. Al and δ containing 16.3 per cent. Al. If the alloy contains less than 11.9 per cent. of aluminium, α begins to form when it is cooled to the appropriate point on line aF . The composition of the α formed is given by the appropriate point on line bc , and as cooling continues, the formation of α proceeds while the composition of the α changes along bc and that of the β along aF . Under equilibrium conditions alloys containing less than 9.8 per cent. Al are completely converted to α before the β reaches F . Thus it is only in alloys that contain more than 9.8 per cent. Al that the formation of α is followed by the eutectoid change. Similar conditions prevail on the other side of the eutectoid point, but if the alloy contains more than 13.4 per cent. Al the transformation of β begins with the formation of γ which changes to δ at 774°C ., and thereafter the transformation continues with the formation of δ until the β reaches point F .

In binary alloys the fineness of the lamellae forming the eutectoid increases with the rate of cooling through the range in which the transformation occurs. The addition of other elements also tends to increase the fineness of the eutectoid structure. Furthermore, the rate of cooling or the addition of other elements makes it possible to obtain eutectoid only in alloys that are not of eutectoid composition, and also to increase the proportion of eutectoid in alloys more remote from the

eutectoid point. In this respect eutectoids resemble eutectics. All these features of eutectoid changes are fully discussed in Chapter XI. Here the mechanism of a eutectoid change will be considered.

When α -iron is forming from γ solid solution, the carbon rejected by the α -iron diffuses into the remaining γ , and when Fe_3C is forming, carbon must diffuse from all over the γ -iron to build up the Fe_3C crystals. When both constituents are forming simultaneously, carbon diffuses away from the α -iron and towards the Fe_3C . If the growing crystals of these two constituents were separated from each other by γ -iron, the diffusion change involved when they were forming together would be equivalent to the sum of the changes involved when they are forming separately. But during the eutectoid transformation plates of α -iron and Fe_3C advance together into the γ as shown in Fig. 174. The alloy illustrated contains less than 0.87 per cent. C. Some α -iron (white) has formed before the eutectoid change begins, and the formation of pearlite commences at the surface of the α -iron and advances into the γ solid solution (black). The lamellae of α -iron and Fe_3C grow side by side and carbon diffuses away from the advancing edges of the α -iron plates and towards the edges of the Fe_3C plates.

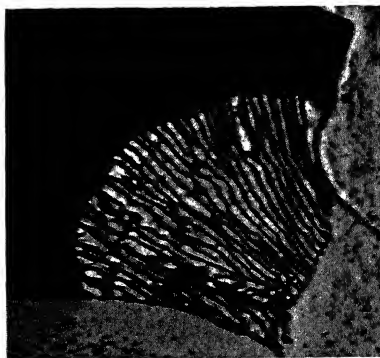


FIG. 174. Formation of pearlite.
× 820.

When α -iron or Fe_3C are present before the eutectoid change begins, it starts at points on the surface of these constituents. If neither of these is present it starts at points on the boundaries of the γ -iron grains. The grains of pearlite are sometimes difficult to distinguish, but in general a grain is a region occupied by one system of parallel plates or by pearlite formed from one centre. Although the grain boundaries of the γ -iron influence the distribution of the points at which the formation of pearlite begins, they do not affect the growth of the pearlite grains, i.e. pearlite exhibits no tendency to spread round the grain boundaries and form envelopes, nor does it develop along crystallographic planes in the γ -iron. The crystallographic orientations of the individual plates of α -iron and Fe_3C are definitely related to the orientations of the γ grains in which they form, but the planes of the plates do not correspond to crystallographic planes in the γ -iron. More often than not the plates are curved. The shapes of the pearlite grains at the completion of the transformation are controlled by the shapes assumed during growth and by the contacts made between different grains or between pearlite and one of the other constituents. The shapes assumed during growth are in turn controlled by the directions in which the plates grow and

this is influenced by the rate of cooling. This question is fully discussed in Chapter XI, and it will suffice to say here that as the rate of cooling is increased the plates tend to an increasing extent to spread out fan-wise from the point at which the formation of the grain began, and thus the external shapes of the grains tend to become more nearly spherical. It is evident therefore that the structural characteristics of a eutectoid are affected by the rate of cooling in quite a different way from those of constituents forming singly. As the rate of cooling is increased, constituents forming singly tend to an increasing extent to grow in one or two directions, thus producing needles or plates, while eutectoids tend to an increasing extent to grow in all possible directions, thus producing spheres.

CHANGES IN ATOMIC ARRANGEMENT

In considering the crystals formed in metals and alloys three aspects of crystal structure may be distinguished. In the first place, there is the space-lattice, i.e. the general arrangement of lattice points or atomic sites in space, and in pure metal crystals this is the only aspect that has to be considered. In primary solid solutions and intermediate constituents, however, two (or more) different sorts of atoms are situated on a common space-lattice and it is necessary to consider (1) the relative numbers of lattice points occupied by the different kinds of atoms, and (2) the way in which these atoms are distributed with respect to each other.

Crystals of pure metals do not occur in alloys, for even when the mutual solubility of the metals is so small that it may for practical purposes be neglected, there is still a sufficient degree of solubility to make the crystals primary solid solutions. Thus two kinds of crystals occur in alloys, namely, primary solid solutions and intermediate constituents, and in both kinds all three aspects of crystal structure have to be taken into account. The phases that occur in alloy systems are distinguished firstly by their space-lattice. A change in space-lattice cannot occur within a phase, and consequently when a lattice change takes place a new phase is formed, e.g., when γ -iron changes to α or when β -Cu-Zn changes to α . Phases are also distinguished by their composition. At both ends of the copper-silver system primary solid solutions with face-centred cubic lattices are formed, but these phases are distinguished by the fact that one is copper-rich and the other is silver-rich. Furthermore, the β -constituents in the alloys of copper with zinc, cadmium, tin, and aluminium all have body-centred cubic lattices, but owing to their different compositions they are different phases. The composition, however, is not such a definite characteristic of a phase as the space-lattice, for variations in composition, i.e. in the relative numbers of lattice points occupied by atoms of different kinds, can occur in a phase. γ -iron, for example, forms a series of solid solutions with nickel, and although the composition, properties, and size of the unit

cell alter progressively, the face-centred lattice persists and the whole range of solid solutions constitute one phase. The same may be said of primary solid solutions in general, and also of many intermediate constituents. Thus β -Cu-Zn at 800° C. can vary in composition between 40 per cent. Zn 60 per cent. Cu and 55 per cent. Zn 45 per cent. Cu, but while the space-lattice remains body-centred cubic the β phase persists. In ternary and more complex systems even greater variations in composition are possible. In the α phase in the Cu-Zn-Al alloys, for example, the relative amounts of the three metals may vary within wide limits and α -Cu-Zn becomes continuous with α -Cu-Al because the space-lattice does not change.

Many intermediate constituents are denoted by formulae, e.g., CuZn, Cu₅Zn₃, &c. These formulae imply definite compositions, but it must be pointed out that in many cases the compositions are not of specific importance. CuZn is a convenient way of stating the composition about which the β -constituent varies, and furthermore, it is convenient to say that this variation takes place by CuZn dissolving zinc or copper. But actually any other composition within the range in which β is stable is equally significant, and zinc or copper atoms in excess of the CuZn ratio are indistinguishable from the others. Thus, although it was explained in Chapter V that body-centred cubic intermediate constituents are formed when the ratio of valency electrons to atoms is 3:2, complex cubic constituents when the ratio is 21:13 and hexagonal constituents when it is 7:4, these exact ratios are not essential and the various space-lattices mentioned should be said rather to form when the ratio of electrons to atoms is approximately 3:2, 21:13, or 7:4.

We have seen that a change in space-lattice always denotes a change in phase, but a change in composition not accompanied by a lattice change does not denote a change in phase unless the composition change is discontinuous. Thus a complete series of copper-nickel alloys consists of the same phase because the composition of the phase varies progressively with that of the alloy. In copper-silver alloys, however, two phases exist, because variations in composition between 0.5 and 99.7 per cent. of copper are accompanied by changes in the relative amounts of two solid solutions of widely different composition and not by a change in the composition of one.

Attention may now be turned to the third aspect of crystal structure, viz. the distribution of two kinds of atoms among the available lattice points. In constituents like CuAl₂, Fe₃C, &c., in which the composition cannot vary, the two kinds of atoms are distributed in a regular manner among the lattice points. But in constituents like those of the CuZn and Cu₅Zn₃ types discussed in Chapter V, the two sorts of atoms may be distributed either in a random or regular manner. Thus in Cu₃Al the two sorts of atoms are distributed on a body-centred lattice in such a way that all the aluminium atoms occupy *D* positions (Fig. 120) while the copper atoms are confined to *A*, *B*, and *C* positions. In Cu₅Sn,

however, no such regular distribution of the two sorts of atoms occurs. Similarly, in Cu_5Zn_8 , Au_5Zn_8 , and Ag_5Zn_8 the two sorts of atoms are distributed in a regular manner on the lattice shown in Fig. 121, but in Cu_5Cd_8 , which has the same type of space-lattice, there is no regularity in the distribution of the two kinds of atoms. Even when a regular distribution of the atoms is realized it is confined to one particular composition in a phase that exists over a range of composition. Thus in Cu_3Al , when aluminium is in excess of the amount required by that ratio, some aluminium atoms occupy *A*, *B*, or *C* positions (Fig. 120), and when copper is in excess, some copper atoms occupy *D* positions. It is therefore evident that a regular distribution of two kinds of atoms among the available lattice points is not a necessary characteristic of a phase. In some types of constituents this condition is always realized, e.g., in those of the CuAl_2 type; in others it is sometimes realized, e.g., in those of the CuZn and Cu_5Zn_8 type, but in these it is only realized at one particular composition in a range of varying composition.

Now while certain constituents always display a regular distribution of the different atoms among the available lattice points, and others always display a random distribution, there are a number of phases in which either random or regular arrangements can be obtained by variations in treatment. In certain primary solid solutions of copper and gold it is possible to convert a random arrangement into a regular or symmetrical one and the question arises whether this is a change in phase. The answer seems to be in the negative, for if the distribution of the atoms among the lattice points is not one of the necessary characteristics of a phase a change in this distribution should not indicate a change in phase. Nevertheless, such changes in the distribution of atoms are accompanied by changes in properties and they are confined to certain limits of composition within the range of a phase. Thus alloys in which a regular distribution of atoms is obtained are distinguished from adjacent alloys in which this condition cannot be realized, and sometimes this is shown in constitutional diagrams just as if a phase change occurred. Furthermore, in some cases the change from a random to an ordered distribution of atoms results in a change in the space-lattice, and under these conditions the distribution change becomes very similar to a phase change. In general, these changes in atomic distribution resemble phase changes in some respects and differ from them in others, and in order to avoid confusion it is advisable to distinguish them from phase changes without putting too much emphasis on the difference.

Copper and gold are mutually soluble in all proportions in the solid state and the constitutional diagram is of the type shown in Fig. 116, i.e. with a minimum in the liquidus curve. Just below the temperature of solidification all the alloys are face-centred cubic primary solid solutions, and the two kinds of atoms are distributed at random among the lattice points. Under all conditions of cooling this state persists

down to about 420°C ., and then in certain alloys an ordered arrangement of the atoms begins to form if cooling is slow. In the face-centred cubic lattice there are four lattice points per unit cell. Each corner atom in the unit cell shown in Fig. 175 is shared by eight cells, consequently the corner atoms make up one lattice point per cell. Each face-centre atom is shared by two cells, consequently the face-centre atoms make up three lattice points per cell. The ratio of face-centre to corner lattice points is therefore three to one, and in an alloy containing copper and gold atoms in this ratio the copper atoms tend to take up face-centre positions and the gold atoms corner positions as the alloy is slowly cooled below 381°C . There is thus a tendency for the lattice shown in Fig. 175 to form, copper atoms being represented by white circles and gold atoms by black circles. In an alloy containing equal atomic proportions of copper and gold a somewhat similar arrangement tends to be adopted, but gold atoms take up the lattice points 1 and 2 in addition to those represented by black circles (thus giving the necessary 50/50 ratio) and the vertical dimension of the unit cell contracts relative to the other two. Thus, when a completely ordered arrangement is obtained, the lattice consists of alternate layers of copper and gold atoms, and as a result of the change in the relative lengths of the sides of the unit cell it becomes tetragonal instead of cubic. In this alloy the change from the disordered to the ordered arrangement begins about 420°C . By water quenching from above this temperature the disordered arrangement is retained, the lattice is face-centred cubic and the length of the side of the unit cube is 3.95 \AA . Slow cooling permits the atomic rearrangement to take place and the space-lattice is then tetragonal, i.e. the sides AB and AC in Fig. 175 remain 3.95 \AA ., but the side AD decreases to 3.65 \AA .

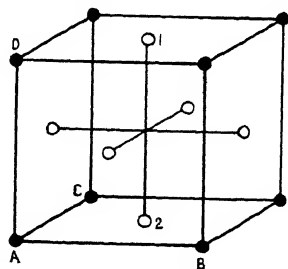


FIG. 175.

The theory of order-disorder changes has been studied by Bragg and Williams (95, 96) and their work is briefly reviewed by Bragg (97). Differences between atoms in a crystal tend to cause atoms of each kind to segregate into certain particular positions and to form an ordered arrangement because such an arrangement has a lower potential energy than one of disorder. Thermal agitation has the opposite effect and tends to produce a disordered arrangement. Thus at lower temperatures ordered arrangements are stable, while at high temperatures thermal movements tend to shuffle the atoms so that the ordered arrangement is lost. If the copper-gold alloy (Cu_3Au) discussed above is in a condition of perfect order (Fig. 175) at a lower temperature, then on heating it will become more and more disordered as the temperature is raised. Transposing a copper atom from a 'right' to a 'wrong' position (i.e. from a position represented by a white circle to one

represented by a black circle in Fig. 175) involves transforming a gold atom from the new position taken up by the copper atom to the position vacated by that atom. In effecting this transposition a certain amount of work is done, and if the amount of work done in transposing two atoms remained constant the change from the ordered to the disordered state would proceed progressively with rising temperature. But the amount of work done is not constant. At first each atom is surrounded by a completely ordered structure, and it must be thrown out of relation to all its neighbours if it moves to a wrong place. Once the change begins, however, certain atoms will have neighbours that are already in 'wrong' positions and this diminishes the work required to move them. As the degree of disorder increases the number of atoms in 'wrong' positions increases and the work required to move atoms that are still in 'right' positions decreases. Thus the change from order to disorder begins slowly, then proceeds at an increasing rate, and finally becomes very rapid after a fairly high degree of disorder has been obtained. Consequently, although the change takes place over a range of temperature, most of it takes place near the upper limit of this range, and this gives rise to the idea of a 'critical temperature' for order-disorder changes. During cooling the reverse change, disorder to order, begins rapidly and then proceeds more slowly, so that while the beginning of the change is comparatively easy to detect its completion cannot be observed.

When heat is applied to an alloy in the ordered condition it supplies the energy required to move atoms from 'right' to 'wrong' positions as well as that required to increase thermal agitation. When an order to disorder change is taking place more heat is therefore required to raise the alloy through a given range of temperature than when no such change is progressing. In other words, the specific heat of the alloy is increased, and the magnitude of this increase depends on the number of atoms changing from 'right' to 'wrong' positions in given temperature intervals. When an order to disorder change begins the specific heat starts to increase, and as the temperature rises it increases at a progressively more rapid rate because of the increase in the rate of the order to disorder change. At the 'critical temperature' of the change the specific heat reaches a maximum, and then it decreases suddenly to a normal value when a completely disordered structure is attained. Fig. 176 (obtained by Sykes (98)) shows the change in specific heat of β -Cu-Zn which undergoes an order to disorder change with a critical temperature at 470° C. An increase in specific heat like that shown in Fig. 176 results in retardation in heating and cooling and is therefore revealed in time-temperature curves. Such arrests during heating and cooling should, however, be distinguished from the absorptions and evolutions of heat that accompany normal phase changes.

At any temperature below the 'critical temperature' the equilibrium

condition of an alloy is one in which the tendency to order arising from differences in the atoms is balanced by the tendency to disorder arising from thermal agitation. The time taken to reach this condition depends, however, on the temperature. At high temperature it is reached rapidly, at lower temperatures slowly, and at still lower temperatures, where atomic interchange ceases, it cannot be reached at all. If the critical temperature of a phase is above the melting-point, as appears to be the case in certain intermediate constituents, then only the ordered condition can be obtained. If it is below the temperature at which atomic movement becomes substantially impossible, only the disordered condition can be obtained. If, however, the critical temperature lies within these limits, the phase will exist in the disordered condition above its critical temperature and in the ordered condition below it. Three cases can then be distinguished. Firstly, the position of the critical temperature may be so related to the freedom of atomic movement in the alloy concerned that the disorder to order change takes place so rapidly that it cannot be suppressed by water quenching. The change in β -Cu-Zn (described later) is of this type. Secondly, the position of the critical temperature may be so related to the freedom of atomic movement that the change may be suppressed by water quenching and permitted to take place by slow cooling. The changes in the copper-gold, iron-aluminium, copper-platinum, and copper-palladium alloys are of this type. Thirdly, the position of the critical temperature may be so related to the freedom of atomic movement that the slowest rates of cooling ordinarily available do not permit the change to take place. This case merges into that in which the critical temperature is below the lowest temperature at which appreciable atomic movement can take place.

All the different conditions described above are arbitrarily selected examples from a continuous sequence. If the critical temperature of a phase is above its freezing-point it is always ordered, if it is below the lowest temperature of atomic movement it is always disordered. If it is within these limits disorder \rightarrow order changes occur, but they are only observed if the rate at which they take place is sufficiently rapid to permit a substantial degree of order to be obtained during cooling at the slowest rates ordinarily available. The tendency towards an ordered distribution of the solute atoms is ascribed above to the difference between the solvent and solute atoms respectively. This difference depends to a large extent on size, and consequently the greater the difference in atomic diameter between the two sorts of atoms concerned the greater will be the tendency for ordered structures to form. As explained in Chapter V, however, a great difference in atomic diameter prevents the formation of solid solutions, and consequently, in so far as

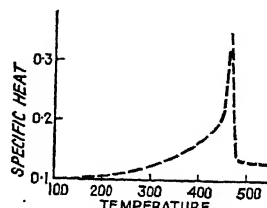


FIG. 176. Specific heat of β -Cu-Zn.

solid solutions are concerned, disorder \rightarrow order changes are only to be expected when the difference in atomic diameter is large enough to promote a tendency to such a change and not large enough to prevent the formation of solid solutions covering a wide range of composition. Consideration of the above factors will show that, although the conditions controlling disorder \rightarrow order changes apply to all phases, the number of phases in which such changes may be observed is comparatively small. So far, the only changes that have been extensively investigated are those in the copper-gold and iron-aluminium solid solutions and in the

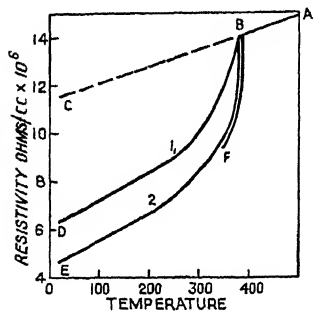


FIG. 177. Resistivity-temperature curves of Cu_3Au .

β intermediate constituent in copper-zinc alloys. Similar changes have been shown to occur in copper-platinum and copper-palladium alloys, and further cases of this kind are suspected in several other systems, e.g. iron-nickel, iron-chromium, and iron-vanadium. (See Chapter XII.)

The progress of the transformation from disorder to order in an alloy containing 75 atomic per cent. of copper and 25 atomic per cent. of gold (i.e. Cu_3Au) has been carefully investigated by Sykes and Evans (99) by means of electrical resistivity measurements. So long as an alloy remains in the same state its electrical resistivity changes gradually with temperature, but when a transformation occurs in the alloy more or less rapid changes in resistivity are observed. During cooling down to 381°C . Cu_3Au undergoes no changes and its electrical resistivity alters along AB (Fig. 177). If cooling below 381°C . is rapid the disorder \rightarrow order change is suppressed and the electrical resistivity continues to alter as before, i.e. along BC . The change from the disordered to the ordered state is accompanied by a decrease in electrical resistivity and the progress of this change during slow cooling can be followed by this means. During cooling at a rate of 30°C . per hour Sykes and Evans found the resistance of Cu_3Au to change along the curve BD (Fig. 177). The shape of this curve shows that the transformation begins rapidly, proceeds at a gradually decreasing rate, and finally ceases at the temperature of the point 1, i.e. 250°C . At this temperature the rate of atomic interchange becomes so slow in relation to the rate of cooling that the disorder \rightarrow order transformation cannot proceed any further. The transformation is not completed, however, and by decreasing the rate of cooling it can be caused to proceed to a greater extent and continue over a wider range of temperature. Thus Sykes and Evans obtained the curve BE by cooling as follows: 500° to 390°C . at 30°C . per hour, 390°C . to 381°C . at 1°C . per hour, then in small steps with periods of soaking so that cooling from 381°C . to 350°C . occupied 100 hours, from 350°C . to 175°C . 100 hours, and from

175° C. to room temperature 6 hours. This curve shows that with the slower cooling the transformation proceeds to a greater extent and continues at a measurable rate down to a lower temperature (point 2). In further experiments the same authors endeavoured to determine the equilibrium conditions at temperatures in the range below the critical temperature. A specimen was heated to 500° C. to produce the disordered state. Then it was cooled to 390° C. at 30° C. per hour and to 381° C. at 1° C. per hour. When the transformation began, the temperature was kept constant until no further change in resistance took place. Further points were obtained by maintaining the alloy at various temperatures until the resistivity reached a steady value, and the values thus obtained when plotted against temperature gave the curve *BF* (Fig. 177). The time taken to determine curve *BF* between 381° C. and 345° C. was 600 hours. It represents the values of resistivity reached at temperatures in this range when the time of heating at each temperature is sufficiently prolonged. With any faster rate of cooling a curve intermediate between *BF* and *BC* is obtained, and *BD* and *BE* are examples of such curves.

It is evident from the above that the disorder \rightarrow order change begins at a definite temperature, that the extent to which it proceeds during cooling through a given temperature interval increases as the rate of cooling decreases, and that the temperature at which the change ceases falls as the rate of cooling decreases. The temperature at which the change begins is easily determined and the approximate temperature at which it stops under given conditions of cooling may also be discovered, but the temperature at which it is completed cannot be ascertained. It is thus quite different from the ordinary phase changes that occur in alloys.

Sykes and Evans found that the change from disorder to order began at certain points in the alloy (i.e. nuclei), and if the temperature was maintained constant just after the change had begun it extended from these nuclei until the whole alloy had attained the condition of order characteristic of that temperature. If, however, cooling was continued it was found that two changes took place concurrently: (1) the transformation extended from the original nuclei, and (2) the degree of order in the transformed regions increased. There are thus two aspects of the transformation: (1) the proportion of the alloy affected, and (2) the degree of order attained in the transformed regions. During continuous cooling these changes take place concurrently. If the alloy is heated for a sufficient time at any given temperature the transformed regions will extend until the whole alloy is affected, but no amount of heating can produce a higher degree of order than is characteristic of that temperature. By quenching specimens of suitable composition from temperatures above and below the critical temperature, Haughton and Payne (100) found that the change from the disordered to the ordered condition in alloys in the neighbourhood of the Cu_3Au composition

was not accompanied by any change in microstructure. In alloys in the neighbourhood of the CuAu composition it was found, however, that specimens which had not undergone the transformation could be distinguished microscopically from those that had, and in specimens quenched while the change was in progress the ordered regions could be distinguished from the disordered. This difference between the Cu_3Au and CuAu transformation evidently arises from the fact that the latter involves a change in space lattice while the former does not. The disorder-order change in alloys of the CuAu composition begins on certain crystallographic planes in the disordered crystals, and plate-like

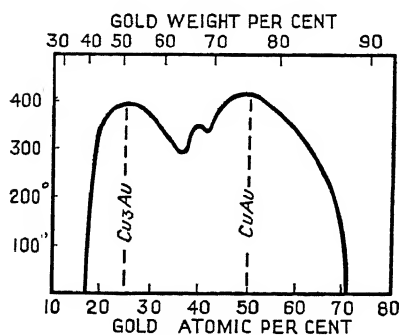


FIG. 178.

ordered crystals parallel to these planes are formed. When the transformation is complete, i.e. when the whole specimen has attained some degree of order, the structure is of the same type as that observed in quenched iron-carbon alloys (Fig. 164) and is described as 'martensitic' by Haughton and Payne. Now while completely ordered structures of the types described above can only be produced in alloys containing the metals in the proportions Cu_3Au or CuAu, other alloys in the neighbourhood of these compositions tend to develop as high a degree of order as their composition permits. As a result the disorder-order changes affect all alloys within a given range of composition. According to Haughton and Payne this range extends from about 18 to 71 atomic per cent. of gold, i.e. from about 40 to 88 per cent. by weight. When the composition of an alloy is not exactly Cu_3Au or CuAu the disorder-order change tends to begin at a lower temperature and consequently the beginning of the transformation in alloys within the range mentioned above is indicated by the curve shown in Fig. 178. The two principal maxima correspond to Cu_3Au and CuAu and the form of the curve connecting them shows that some degree of order is attained in all intermediate alloys. A small maximum occurs at Cu_3Au_2 and Haughton and Payne suggest that at this composition a third type of ordered structure may be formed.

Changes from disorder to order are accompanied by changes in properties, notably in specific heat and electrical resistivity, but sometimes also in hardness and other mechanical properties. As a result of this the hardness and resistivity of copper-gold alloys at atmospheric temperature depend on whether the alloys are slowly cooled from 400°C. or quenched from above this temperature. Fig. 179, which is based on the work of Kurnakow, Zemczuzny, and Zasedatelev (101), shows the results of hardness and resistivity measurements on quenched

and slowly cooled alloys respectively. In the quenched alloys the properties vary gradually with composition in the manner characteristic of primary solid solutions. In the slowly cooled alloys the formation of the ordered structures results in discontinuities in the curves. In the resistance curve there are two minima corresponding to Cu_3Au and CuAu respectively. In the hardness curve there are minima at these particular compositions but maxima on each side of them. This applies particularly to alloys in the neighbourhood of the CuAu composition, and although an alloy containing exactly 50 atomic per cent. of gold is not much harder in the slowly cooled than in the quenched condition, alloys containing 45 and 55 atomic per cent. are affected to a pronounced extent by the rate of cooling.

The formation of ordered structures in iron-aluminium alloys has been studied by Bradley and Jay (102). Alloys containing up to 34.5 per cent. aluminium solidify as primary solid solutions of aluminium in α -iron. The solubility decreases with temperature and is 33 per

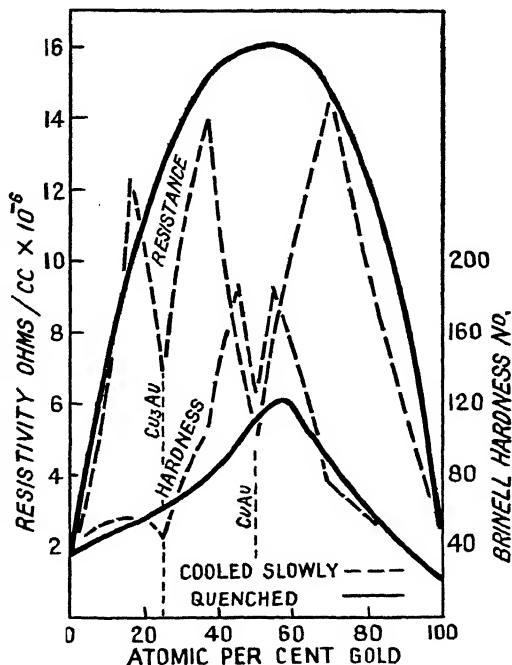


FIG. 179. Resistance and hardness of Cu-Au alloys.

cent. at atmospheric temperature. Alloys containing less than 1 per cent. aluminium change to γ , then revert to α , in the same way as the iron-phosphorus alloys containing less than 0.55 per cent. phosphorus (Fig. 170), but apart from this change all alloys containing up to 33 per cent. aluminium may be regarded as primary solid solutions of aluminium in α -iron. As the proportion of aluminium is increased from 0 to 9.9 per cent., aluminium atoms replace iron atoms in a random manner on the body-centred cubic lattice. Above this percentage an ordered arrangement begins to form in slowly cooled alloys. The aluminium atoms tend to take up positions on one of the four interpenetrating face-centred lattices of which the body-centred lattice may be supposed to be made up. In other words, all the aluminium atoms tend to take up *C* positions in Fig. 120. At 13.9 per cent. aluminium (i.e. 25 atomic per cent.) nearly all the aluminium atoms are in *C* positions and all the *A*, *B*, and *D* positions are occupied by iron atoms.

Thus an ordered structure of the composition Fe_3Al is formed. As the aluminium content is increased above this amount, atoms of this element begin to take up *D* positions, and between 13.9 and 23 per cent. the number of atoms in *C* positions decreases while the number in *D* positions increases. At 23 per cent. aluminium there is an equal number of atoms in *C* and *D* positions; then as the aluminium content is further increased the atoms of this element begin to fill the remainder of the *C* and *D* positions. At 32.6 per cent. aluminium (50 atomic per cent.) all the *C* and *D* positions are occupied by aluminium atoms and an ordered structure of the composition FeAl is formed. In slowly cooled alloys therefore the formation of an ordered structure begins at 9.9 per cent. aluminium and is completed at 13.9 per cent., above this proportion the transition from the Fe_3Al to the FeAl structure proceeds and is completed at 32.6 per cent. The lattice of Fe_3Al is similar to that of Cu_3Al and the lattice of FeAl is similar to that of CuZn . If the iron atoms in FeAl are assumed to contribute no valency electrons to the structure this composition gives the 3 : 2 ratio of electrons to atoms (see Intermediate Constituents, Chapter V). To obtain this ratio in Fe_3Al it is necessary to suppose that each iron atom contributes one electron, giving 6 electrons to 4 atoms. Thus Bradley and Jay suggest that between FeAl and Fe_3Al the effective valency of the iron changes from zero to one.

When iron-aluminium alloys are quenched from above 600° C. the structure remains random up to 14 per cent. aluminium. At this composition there is a sudden change to an ordered structure in which all the aluminium atoms are in *C* and *D* positions (Fig.120). As the aluminium content is further increased the aluminium atoms fill the remainder of the *C* and *D* positions until at 32.6 per cent. aluminium the perfect FeAl structure is obtained. Raising the quenching temperature to 1,000° C. does not substantially affect the results obtained, and it may therefore be inferred that in alloys containing more than 14 per cent. aluminium either the FeAl type of structure is formed above 1,000° C. or its formation is not prevented by quenching.

The lattice spacing, i.e., the length of the side of the unit cube, varies with the composition and the treatment. In both quenched and slowly cooled alloys it increases linearly with the aluminium content up to 9.9 per cent. In slowly cooled alloys it then remains constant from 9.9 to 17 per cent., decreases slightly from 17 to 20 per cent., and then increases progressively but not linearly up to 32.6 per cent. In quenched alloys the lattice spacing continues to increase above 9.9 per cent. of aluminium, but not so rapidly as below this proportion. At 14 per cent. aluminium there is a sudden decrease in the lattice spacing which then remains substantially constant up to 20 per cent. and rises like that of slowly cooled alloys from 20 to 32.6 per cent. It is therefore evident that the lattice spacing depends not only on the relative proportions of the different kinds of atoms present, but also on the way in which they

are arranged with respect to each other on the common lattice. From this it follows that curves connecting composition and lattice spacing, density, or specific volume should show discontinuities where ordered arrangements are formed, and curves connecting temperature and volume should show discontinuities in the ranges in which order-disorder transformations occur.

The physical properties of iron-aluminium alloys in the range 0-17 per cent. aluminium have been studied by Sykes and Evans (103) and Sykes and Bampfylde (104). The former investigators found that the change from the disordered to the ordered structure in an alloy containing about 14 per cent. aluminium (Fe_3Al) began at 500°C . and proceeded in the same way as that in Cu_3Au , i.e. at each temperature below 500°C . a certain degree of order is attained if sufficient time is allowed, but further heating at this temperature does not permit any higher degree of order to be established. During continuous cooling at the equilibrium rate the change proceeds as the temperature falls. Slower cooling has no effect, but more rapid cooling decreases the extent to which the change proceeds in each temperature interval. The disorder-order change was found to have little influence on hardness and tensile strength but the electrical resistivity was notably affected. Thus in alloys containing up to about 11.5 per cent. aluminium the resistivity increased linearly with the aluminium content and was not affected by the rate of cooling. Above this amount the resistivity of quenched alloys continued to increase with aluminium content along a curve that was approximately a continuation of that representing resistivity up to 11.5 per cent. In slowly cooled alloys, however, the resistivity began to decrease above 11.5 per cent. aluminium, reached a minimum at 14 per cent. (Fe_3Al), then increased rapidly and approached the value for quenched alloys at 17 per cent. aluminium.

The β -constituent in the copper-zinc alloys undergoes a transformation at 470°C ., which is shown in the diagram of this system (Fig. 513, Chapter XV). This transformation has been the subject of a number of investigations and several different explanations have been suggested. It is now generally agreed, however, that the transformation in question is a disorder \rightarrow order change in the β -lattice. This explanation was first proposed by Tammann and Heusler, it was accepted and emphasized by Bragg (105), shown to be consistent with the results obtained by Sykes (98) and Owen and Pickup (106), and finally verified experimentally by Jones and Sykes (596) who detected the ordered structure by X-ray analysis. Above 470°C . the copper and zinc atoms are distributed at random on the body-centred lattice, below 470°C . an ordered arrangement is formed, and the zinc atoms tend to take up *C* and *D* positions (Fig. 120), while the copper atoms take up *A* and *B* positions. The change in the atomic arrangement is accompanied by a change in specific heat, as shown in Fig. 176, and may therefore be detected by means of cooling curves. Sometimes the ordered structure stable

below 470° C. is referred to as β^1 to distinguish it from the disordered β structure stable above 470° C.

CONSTITUTION, STRUCTURE, AND PROPERTIES

In Chapters III and IV the behaviour of metals subjected to stress was considered in relation to pure metals from the point of view of the effects of the nature and magnitude of the stress, time, and temperature. The effects of crystal size and differences between one pure metal and another were taken into account, and these are the only constitutional variables that arise in connexion with pure metals. In alloys, however, several other variables are introduced. Like pure metals they may consist of crystals of one kind only, and these may be either primary solid solutions or intermediate constituents. If the crystals are primary solid solutions the mechanical properties will resemble to some extent those of the basis metal, but this does not apply to chemical and electrical properties. If the crystals are intermediate constituents none of the properties may resemble those of the component metals. Frequently, however, alloys consist of crystals of more than one kind, and then the properties depend on those of the various constituents present, their relative amounts, the sizes of the crystals, and the way in which they are arranged with respect to each other. It is the purpose of this section to consider generally and briefly the effect of variations in constitution and structure on mechanical properties and factors relating to them, and also to deal shortly with electrical properties. For convenience, primary solid solutions, intermediate constituents, and eutectics (or eutectoids) will first be dealt with separately, and then the various types of structure composed of two or more constituents will be considered.

Although this section is concerned with the relations between constitution, structure, and properties, it is necessary to explain that these cannot be isolated from the other factors that affect properties. As indicated in the chart shown in Chapter I, the properties are related to the nature of a metal (i.e. its composition, condition, constitution, microstructure, and crystal structure) and the last four are in turn related to composition and treatment (i.e. casting, hot-working, cold-working, and heat treatment). To a large extent the treatment influences the properties by affecting the constitution and structure. Thus a sand casting and a chill casting of the same composition have different microstructures and sometimes different constitutions. Annealing a casting (heat treatment) promotes constitutional and structural changes, hot-working refines the crystal size and changes the distribution of the constituents, cold-working alters the shape of the crystals and breaks up brittle constituents, and heat treatment involving cooling at different rates or heating to different temperatures has numerous effects on constitution and structure. These effects of treatment may be taken into account when dealing with constitution

and structure, but in so far as treatment influences condition it cannot be dealt with in this way. The casting conditions (and the melting conditions that precede casting) influence the soundness and quality of a metal, i.e. the size, number, and distribution of the cavities caused by the liberation of gas or contraction of the metal, and of non-metallic particles included in the solid metal. Samples of metals that are otherwise identical will have very different properties if they contain different amounts of cavities and inclusions. Furthermore, the casting conditions influence the amount of internal stress produced in the solid metal, and this in turn affects the properties. Annealing a casting, besides promoting constitutional and structural changes, serves to relieve internal stress, while hot-working, besides altering the structure, tends to consolidate the metal by closing the cavities and to alter the shape and distribution of the inclusions. Hot-working may lead, however, to the development of internal stress, and consequently annealing after hot-working relieves this besides promoting structural changes. Cold-working produces a substantial alteration of properties accompanied by change in structure and the development of internal stress. Heating after cold-working may alter these properties and relieve the stress to some extent without appreciably affecting the structure, or, alternatively, it may completely change the structure and properties and relieve all the stress. Finally, heat treatment, besides producing constitutional and structural changes, may either give rise to or eliminate internal stress according to (1) the nature of the metal concerned, (2) the size of the piece treated, and (3) the rates of heating and cooling and time and temperature of heating. Besides all the factors mentioned above, the properties of a metal may be affected by the type of atmosphere in which it is heated for annealing, hot-working, or other heat treatment.

It is evident that even when constitution and structure are exactly defined in terms of the constituents present, the size of the crystals and their relative distribution, numerous factors that affect the properties have still to be taken into account. These factors are considered generally in Part IV and particularly in Parts V and VI. Meanwhile, it is necessary to describe the relations between structure, constitution, and properties without taking account of gas or contraction cavities, inclusions, internal stress, or the superficial effects of the atmosphere to which the hot metal has been exposed. In general terms this can be done without difficulty, but when actual figures are given to illustrate the properties of a given alloy it must be remembered that these are affected by the factors just mentioned, and while their relative significance may not be questionable, no absolute value may attach to them.

Primary Solid Solutions.

In general when an element dissolves in solid solution in a basis metal the resistance to deformation, the rate of strain-hardening, the

recrystallization temperature, and the electrical resistivity of the basis are all increased. The increase in resistance to deformation and rate of strain-hardening leads to an increase in tensile strength and hardness, but the elongation and reduction in area of primary solid solutions are affected by a number of factors which are generally considered in Chapter III. Thus the total amount of deformation that a specimen undergoes before fracture occurs in a tensile test depends on the relations between the rate of strain-hardening and the breaking stress. When the metal has been strain-hardened to such an extent that the resistance to deformation exceeds the breaking stress, fracture occurs. This total deformation is the only factor that affects the reduction in area, but the elongation consists of two portions, the uniform extension that takes place while the rate of strain-hardening is greater than the rate of reduction in area, and the local extension that takes place when the conditions are reversed. When one element forms a primary solid solution in another it tends to decrease the reduction in area and the local extension by increasing the rate of strain-hardening, but it may also tend to increase these by increasing the breaking stress. Under the same conditions the added element tends to increase the uniform extension by increasing the rate of strain-hardening, and this is likely to continue until strain-hardening becomes so pronounced that fracture takes place before local extension begins. In general, therefore, the reduction in area, total elongation, and uniform elongation of a primary solid solution may either be greater or less than that of the pure basis metal.

Various examples of the effects on the mechanical properties of copper of elements that form solid solutions with it are discussed in Chapter XV. Fig. 527 (p. 1292) illustrates the effect of zinc content on the Brinell hardness of copper-zinc alloys and it will be seen that within the range of the primary α solid solution (i.e. up to about 36 per cent. of zinc in this case) the hardness number increases from 40 in pure copper to 57 in an alloy containing 20 per cent. of zinc and then remains substantially constant until the β -constituent appears. Fig. 528 illustrates the effect of the zinc content on the tensile strength, and here, within the α range, the strength increases from 14 to about 16 tons per sq. in., as the zinc content rises from zero to 20 per cent. In this range the elongation also rises, i.e. from 45 per cent. in pure copper to 65 per cent. with 30 per cent. of zinc as shown in Fig. 529. In Fig. 544 the effect of tin is shown, and it will be seen that the tensile strength and hardness rise with the tin content while the elongation falls. In this case the limit of the primary α solid solution is difficult to determine. Under equilibrium conditions it extends to 16 per cent. of tin and then a eutectoid of $\alpha + \delta$ similar to that formed in the copper-aluminium alloys makes its appearance. Usually, however, this is formed at much lower tin contents, and in the alloys used for the hardness determinations in Fig. 544 it appears at about 12 per cent. tin, while in those

used for the tensile strength and elongation curves it occurs at about 7 per cent. The change in tensile strength and elongation between 0 and 7 per cent. may therefore be attributed to the effect of tin dissolved in copper. Fig. 545 shows the effect of aluminium, and here the primary α solid solution extends up to 7 per cent. aluminium. In this range the tensile strength increases from 11 to 19 tons per sq. in., while the elongation rises from 40 to 78 per cent.

Some values for the mechanical properties of copper and the solid solution of zinc in copper are given below as determined by Cook and Larke (598).

TABLE 25

	<i>Pure Cu</i>	<i>95% Cu 5% Zn</i>	<i>70% Cu 30% Zn</i>	<i>64% Cu 36% Zn</i>
Tensile strength tons per sq. in. .	15.7	16.3	20.9	21.2
Elongation % on 0.75 in. . . .	61.0	58.7	81.8	77.2
Elongation % on 2 in.	46.3	44.3	67.1	65.3
Elongation % on 7 in.	38.1	34.9	60.3	58.5
Uniform elongation %	35.4	31.7	57.6	56.2
Reduction in area%	61.8	78.2	68.6	65.8

It will be seen that the tensile strength increases with the zinc content, and that the reduction in area increases to a maximum with 5 per cent. of zinc and then diminishes. The uniform extension decreases to a minimum at 5 per cent. of zinc and then rises substantially. The figures for total elongation indicate how this depends on the gauge length, becoming smaller as the gauge length increases and the effect of the local extension becomes less pronounced. These figures also show that whereas the addition of 5 per cent. of zinc decreases the total elongation the addition of 30 or 36 per cent. increases it substantially.

The effect of various elements that form primary solid solutions with α -iron has been studied by Rees (107), and in the following table some of the results obtained are shown compared with the mechanical properties of pure iron.

TABLE 26

<i>Alloy</i>	<i>Tensile strength tons sq. in.</i>	<i>Elongation % on 2 in.</i>	<i>Brinell hardness</i>
Pure Iron .	16	48	67
2.2% Si .	33.6	38	164
3.85% Si .	40.5	6	218
4.7% Si .	40.5	Nil	261
6.5% W .	29.4	37	145
10.1% W .	30.8	36	149
3.95% Mo .	30.8	34	154
6.0% Mo .	31.2	28	158
2.9% V .	20.8	48	101
6.0% V .	22.8	10	132

When the two metals forming a primary solid solution are soluble in each other in all proportions it is to be expected that at each end of the

system the effect of adding one metal to the other will be observed so that the strength and hardness should rise to a maximum at some intermediate composition. This is shown for the hardness of copper-gold alloys by the full line curve in Fig. 179. It is further shown for the copper-nickel alloys by the figures for tensile strength and hardness in Table 27. Here the tensile strength and hardness of copper are shown to be raised by the addition of nickel and the corresponding properties of nickel to be raised by the addition of copper so that a maximum is reached at 60 per cent. of nickel. The elongation and reduction in area reach a minimum at 40 per cent. of nickel.

TABLE 27

Mechanical Properties of Copper-Nickel Alloys (597).

<i>Nickel content</i>	<i>Tensile strength tons/sq. in.</i>	<i>Elongation %</i>	<i>Reduction in area %</i>	<i>Brinell hardness</i>
0	14.8	53.0	85.0	36.5
10	17.4	47.0	69.0	51.1
20	19.7	43.0	62.4	58.2
30	22.3	40.3	57.0	67.0
40	24.0	39.0	55.0	70.8
50	25.2	41.0	56.5	73.5
60	26.7	41.0	58.5	74.3
70	26.4	42.0	66.0	73.2
80	25.1	43.1	65.0	68.1
90	24.1	45.5	66.0	61.5
100	21.6	48.5	81.5	54.2

It will be seen from the examples described above that primary solid solutions tend in general to be harder and stronger than the metals on which they are based, but the effect of the added element on the ductility varies in different cases. Thus 3.85 per cent. of silicon dissolved in α -iron raises the tensile strength from 16 to 40.5 tons per sq. in., and decreases the elongation from 48 to 6 per cent., while 10 per cent. of tungsten only raises the strength to 30.8 tons per sq. in., and lowers the elongation to 36 per cent. Aluminium or tin in solid solution in copper increases the tensile strength to a marked extent, but zinc is much less effective, and whereas the elongation definitely increases with the aluminium and zinc content it does not increase with the tin content. When the two metals form a continuous series of solid solutions, the strength and hardness increase to a maximum at some intermediate composition. In the copper-nickel alloys given as an example the elongation and reduction in area fall to a minimum, but in view of the other results given for the ductility of primary solid solutions, it is evident that this is not a necessary feature of systems of this type. It may be added that the increase in strength produced when a given total amount of solute is present is greater when this total is made up of several elements instead of one as in binary alloys. For this reason, as will be shown in Chapter XV, complex alloys are generally used when high strengths are required.

Although zinc in solid solution in copper does not greatly increase its ultimate tensile strength, it substantially increases its capacity for strain-hardening by cold-working. Thus, pure copper, which has a tensile strength of about 15 tons per sq. in. in the hot-rolled and annealed condition, may be strain-hardened to a strength of about 30 tons per sq. in., by a reduction in area of 95 per cent. in wire drawing (Fig. 509), while α -brass (67 per cent. Cu 33 per cent. Zn) may have its strength increased from 23 to 62 tons per sq. in. by the same treatment (Fig. 532). Similar conditions are realized in solid solutions generally, and in most cases much smaller amounts of the solute element have much larger effects on the strain-hardening capacity. In the cast conditions the crystals of primary solid solution are heterogeneous as a result of the selective freezing that accompanies solidification. They may be made homogeneous by annealing, but the effect of this on the properties is masked to some extent by the relief of internal stress. In general, however, annealing may be said to produce a certain amount of softening, and this is shown for copper-zinc alloys in Fig. 530. As in the case of pure metals and alloys generally, the mechanical properties of primary solid solutions vary with the crystal size, i.e. as this decreases the resistance to deformation increases. This is shown for pure iron in Figs. 48-50, Chapter III.

The conditions under which the strain-hardening produced by deformation is eliminated are very important characteristics of metals. They determine the temperature to which a metal must be heated to soften it after cold-working operations and also the temperature range in which it may be used for purposes of construction. At temperatures at which strain-hardening is eliminated slowly or not at all a metal may be used for constructional purposes, but at those at which it disappears rapidly it cannot be used. As explained in Chapter IV, the removal of strain-hardening is closely related to recrystallization, and consequently the recrystallization temperature (i.e. the lowest range of temperature in which recrystallization takes place rapidly after severe working) is a good indication of the permanence of strain-hardening. This temperature is raised by elements in solid solution and the effects are most marked when the first small amounts are added.

Using aluminium of commercial purity (about 98.5 per cent. Al) Carpenter and Smith (108) found that on heating after severe working new crystals began to appear at 150° C. Recrystallization at this temperature was slow, however, and the authors calculated that 10 years would be required for it to proceed to completion. The temperature had to be raised to 300° C. before recrystallization took place rapidly (i.e. in 30 minutes) and the softening, after working, of commercial aluminium is carried out in the range 300-350° C. Using aluminium of high purity, cold-worked as described in Chapter V, Calvet (593) found that in a sample containing 99.9986 per cent. of aluminium softening was completed in 6 to 10 minutes at 100° C. and

that even at 16° C. softening was comparatively rapid. A less pure sample containing 99.997 per cent. of aluminium was not completely softened after 6 hours at 100° C., and when the purity was reduced to 99.996 per cent. only a small amount of softening occurred in 240 hours at 100° C. The complete annealing of this sample required 48 hours at 175° C. A still more impure sample containing 99.96 per cent. of aluminium was incompletely softened after 100 hours at 225° C. Very small amounts of soluble impurities raise the recrystallization temperature notably, and observation of this temperature is sometimes used as a method of determining the degree of purity of metals of high quality. A good example of the effect of a small quantity of a soluble element on recrystallization is provided by tellurium in lead. The mechanical properties of lead at atmospheric temperature are influenced to a great extent by the fact that it can recrystallize at this temperature. The addition of as little as 0.06 per cent. of tellurium prevents this and leads to a marked improvement in mechanical properties. This is discussed more fully in Chapter XVI.

The temperature at which a metal recrystallizes after working depends on the amount of this—and the duration of heating. Thus even when the composition is fixed the recrystallization temperature is determined by these factors. In Chapter XV this is fully considered in connexion with copper, and it is shown that when the metal contains a minimum amount of soluble impurities, and is reduced in area more than 50 per cent. by wire drawing, recrystallization takes place between 130° and 330° C. according to the amount of deformation and the time of heating. Elements in solid solution raise the recrystallization range, but in order to show their exact effect it would be necessary to perform a systematic investigation on the effects of the amount of deformation and the time and temperature of heating for different amounts of each element. This has not been done, but some important information, which is considered in detail in Chapter XV, has been accumulated. 0.24 per cent. of silver raises the recrystallization temperature of copper from 205° to 340° C. 0.09 per cent. of arsenic raises it from 250–300° C. to 300–350° C., while 1 per cent. raises it to 350–400° C. 0.47 per cent. of antimony raises it from 250–300° to 350–450°, while 2.09 per cent. of iron raises it from 210° to 300° C. Only about 0.2 per cent. of iron is soluble in copper at room temperature under equilibrium conditions.

The electrical resistivity of a pure metal is very greatly increased by the addition of a second element with which it forms a solid solution. The resistivity curve represented by the full line in Fig. 179 is typical of the conditions produced in the case of two metals mutually soluble in all proportions. The resistivity of each metal is raised by the addition of the other and a maximum resistivity is attained at an intermediate composition. A similar curve for the copper-nickel alloys is shown in Fig. 566, Chapter XVI. As will be seen in Fig. 179, the increase in resistivity is approximately a linear function of the composition when

the amount of added element is small, and thus lines like those shown in Fig. 512 may be drawn to represent the effect of different elements on the resistivity of a given pure metal. In this figure the basis metal is copper, and the effect on the resistivity of the addition of small amounts (up to 0.6 per cent.) of various elements is shown. Of these, oxygen is soluble to the extent of less than 0.007 per cent. at atmospheric temperature, and the solubility of bismuth is even smaller. The curve for iron indicates a solubility of 0.4 per cent. in the specimens used. The other elements are all soluble within the limits covered by Fig. 512 and their effect on the resistivity increases in the order Ag, Cd, Zn, Ca, Ni, Sn, Al, Mn, As, Si, P. The increase in resistivity caused by the addition of one metal to another is accompanied by a decrease in the temperature coefficient of resistance and this is shown in Fig. 566. The thermal conductivity changes in the same way as the electrical conductivity and the two changes are closely related as shown by Smith and Palmer (599).

The broken resistivity curve in Fig. 179 shows that the resistivity decreases when the copper-gold alloys change from the disordered to the ordered state, and minima occur at the compositions Cu_3Au and CuAu . The electrical resistivity of ordered iron-aluminium solid solutions is also lower than that of the disordered, and the same applies to copper-palladium and other alloys that undergo changes of this kind. As will be shown in the next section, minima on the composition-resistivity curves also appear at the basis compositions of intermediate constituents, e.g. AuZn , and this is clearly another point of similarity between ordered structures and intermediate constituents.

Intermediate Constituents.

The intermediate constituents that occur in the alloy systems considered in this book may be divided into four types, as follows:

Type 1. The crystal structure is similar to that of pure metals and primary solid solutions (i.e. face-centred or body-centred cubic). The composition can vary over an appreciable range, and the properties are similar to those of pure metals and primary solid solutions. Examples are the β -constituents in the alloys of copper with zinc, aluminium, and tin.

Type 2. The crystal structure is more complex than that of pure metals and primary solid solutions, and the properties are quite different. The composition can vary over a range. Examples are the γ -constituent in copper-zinc alloys and the δ -constituents in copper-tin and copper-aluminium alloys.

Type 3. Similar to Type 2 except that the composition cannot vary. Examples are CuAl_2 , Mg_2Si , FeAl_3 .

Type 4. Similar to Type 3 except that one of the components is not a metal. Examples are carbides such as Fe_3C , Cr_3C_2 , nitrides such as Fe_4N , and phosphides such as Fe_3P and Cu_3P .

The β -constituents in the copper-tin and copper-aluminium systems are high-temperature phases, but at the temperatures at which they exist their properties are similar to those of β -Cu-Zn. This last is harder than the α -Cu-Zn, and consequently property-composition curves show an increase in strength and hardness and a decrease in elongation when it appears. This is indicated in Figs. 527, 528, and 530. The rapid increase in tensile strength above 35 per cent. of zinc in Fig. 528 and

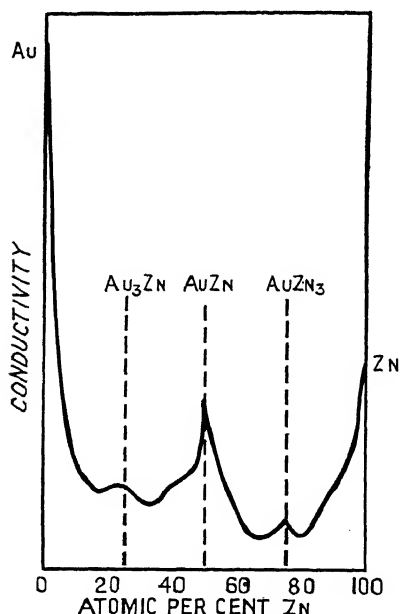


FIG. 180.

the rapid fall in elongation above 32 per cent. of zinc in Fig. 529 are due to the appearance of β , and the maximum on the tensile strength curve at 45–48 per cent. of zinc may be regarded as representing the tensile strength of this constituent. Thus, while the tensile strength of copper is between 14 and 15 tons per sq. in., and that of α -Cu-Zn between 15 and 18 tons per sq. in., the strength of β is between 30 and 32 tons per sq. in.

The electrical conductivity of copper-zinc alloys decreases with the zinc content in the range of the α solid solution in the manner described in the previous section. When β appears, however, it begins to increase, and a maximum value (minimum resistivity) is reached at 49–50 per cent. of zinc (CuZn contains 50.7 per cent. of zinc). Similar maxima

are usually obtained at the composition approximating to the basis composition of intermediate constituents, and Fig. 180, taken from Hume-Rothery (10) and based on the work of Soldau (111), illustrates how the conductivity varies with composition in systems in which intermediate constituents are formed.

The other types of intermediate constituents are all characterized by their great hardness and brittleness in comparison with the common ductile metals and primary solid solutions based on them, e.g. the Brinell hardness of pure iron is about 63 while that of Fe_3C is about 820. The effect on the mechanical properties of a constituent of this kind is shown in Figs. 527, 528, and 529. When γ appears in copper-zinc alloys the hardness continues to increase as shown by the upper curve in Fig. 527 and the elongation to decrease as shown in Fig. 529. Owing to the brittleness induced by the presence of this constituent, the tensile strength does not rise with the hardness but falls with the elongation as shown in Fig. 528. In this figure γ appears at about 45–46 per cent. of

zinc and as the amount increases the strength falls rapidly. The curves do not extend to the zinc content necessary for the production of alloys consisting entirely of γ , but it is evident that at this composition the tensile strength would be almost zero. These three figures representing the properties of copper-zinc alloys illustrate in a general way the meaning of the terms ductility, toughness, and brittleness. In the α range the alloys are ductile, i.e. the strength and hardness are low and the elongation is high. When β appears the ductility begins to change to toughness, i.e. the strength and hardness increase while the elongation decreases. When γ appears the toughness begins to change to brittleness, i.e. the hardness continues to increase but the strength and elongation decrease. Most of the intermediate constituents of the γ -Cu-Zn, CuAl₂ and Fe₃C types are so brittle that alloys consisting entirely or mainly of them break up rather than deform when subjected to mechanical forces.

Eutectics and Eutectoids.

These constituents are composite and not homogeneous like those previously described. Their mechanical properties are therefore influenced by the factors that affect the properties of aggregates, and in considering them account must be taken of the properties of the two constituents present, the relative proportions in which they occur, the size of the crystals, and the way in which they are arranged with respect to each other.

If both constituents are brittle the eutectic or eutectoid as a whole will be brittle, while if both are tough or ductile it will be tough or ductile and will show the effects of the relatively small grain-size of constituents of this type. If, however, one of the constituents is ductile and the other brittle, then the properties of the whole will be influenced to a pronounced extent by the factors mentioned above. This is the kind of eutectic or eutectoid that is of greatest practical importance, for industrial alloys used on account of their mechanical properties belong in general to one of the following types:

1. Those consisting of a primary solid solution or of a primary solid solution and an intermediate constituent of the β -Cu-Zn type.
2. Those consisting of a pure metal or a primary solid solution and a eutectic or eutectoid in which the second constituent is a hard and brittle intermediate constituent of the CuAl₂ or Fe₃C type.
3. Those consisting of unstable solid solutions retained at atmospheric temperature by rapid cooling or of structures resulting from the partial or complete decomposition of these solid solutions at relatively low temperatures.

In dealing with alloys that consist of two constituents of very different properties two points must be borne in mind. The first is that the continuous constituent exercises a controlling influence on the

mechanical properties, and the second is, providing that the alloy can be deformed without fracture, the deformation tends to break up the brittle constituent and establish the continuity of the ductile one. The most important constituent of the type under consideration is 'pearlite', which is a eutectoid consisting of alternate plates of Fe_3C and ferrite (i.e. α -iron containing small amounts of carbon and usually larger amounts of other elements in solid solution). The hardness of ferrite is about 90 Brinell, and that of Fe_3C 820 Brinell. Pearlite contains about 0.9 per cent. of carbon, i.e. 13.6 per cent. Fe_3C and 86.4 per cent. of ferrite. Owing to the predominance of the ferrite it tends to be the continuous constituent, but this continuity is not very evident in undeformed pearlite. When a steel containing about 0.9 per cent. of carbon is slowly cooled from the austenite range (Fig. 168) the plates of Fe_3C are relatively thick and it is difficult to deform the metal to an appreciable extent without causing fracture through them. In a tensile test the strength is comparatively high but the elongation and reduction in area are low. As the rate of cooling from the austenitic range is increased the plates of Fe_3C become finer and the strength, elongation, and reduction in area all increase, i.e. the alloy becomes tough instead of comparatively brittle. Large quantities of wire are made by cold drawing steel containing this amount of carbon after cooling at a rate that produces thin plates of Fe_3C . If these plates are thick they cannot be deformed without rupture, and when this happens the resulting fracture is large enough to provide a starting-point for a crack that extends throughout the cross-section of the metal. When the plates are thin, however, and supported on both sides by ductile plates of ferrite, they bend when the metal is deformed and when they break the fractures are small. As the breaking up of the brittle plates proceeds the structure becomes more and more capable of deformation, but this is offset by the strain-hardening of the ferrite. Most of the deformation occurs in this constituent, and as the plates or particles of Fe_3C tend to prevent its easy flow, it is hardened to a greater extent by a given amount of deformation than if the carbide was absent. Thus after the initial stages of deformation are past and the plates of Fe_3C are broken up to the requisite extent the capacity for further deformation depends on the rate of strain-hardening of the ferrite matrix. Steels in this condition cannot be deformed to the same extent as pure iron, but their strength may be increased to a remarkable degree by wire drawing, and from steel that has a tensile strength of 60–70 tons per sq. in., when appropriately cooled, wire with a tensile strength of over 200 tons per sq. in. can be manufactured.

If, after a certain amount of deformation has been performed on pearlite, it is heated to a temperature above 600°C . and below 715°C . (at which it may begin to change to austenite) the broken plates of Fe_3C readily change into globules under the action of surface tension. The structure then consists of isolated globules of Fe_3C in a matrix of

ferrite and the steel is in a condition favourable to deformation. As before, the deformation takes place almost entirely in the ferrite, but the presence of the hard globules increases the resistance to flow and the amount of strain-hardening caused by a given amount of deformation.

The Brinell hardness (and the other mechanical properties) of pearlite depends on the fineness of the plates. According to Belaiew (112) the interlamellar distance in normal pearlite obtained by slow cooling is between 0.4 and 0.26μ and the hardness lies between 200 and 325 Brinell. In fine pearlite obtained by more rapid cooling the interlamellar distance is 0.26 – 0.1μ and the hardness 325–450 Brinell. This increase in hardness is accompanied by an increase in strength without a corresponding decrease in ductility.

As already explained the mechanical properties of alloys consisting of two constituents depend on the properties of these constituents, the relative amounts present, the size of the crystals and their arrangement with respect to each other. Electrical conductivity is influenced by the same factors. In an alloy of eutectic or eutectoid composition the two constituents are present in definite proportions, they are arranged in a certain way with respect to each other, and the crystals are relatively small. All these features may be affected by the rate of cooling or subsequent deformation, but an alloy of this composition differs in certain important respects from alloys on each side of it. If, when the eutectic composition is departed from, primary crystals of a solid solution make their appearance, then the eutectic matrix will be interspersed with skeleton crystals. The exact structure produced depends on the relative proportions of skeletons and eutectic and on several other factors, but it represents a marked deviation from the structure that consists entirely of eutectic. The same may be said about the conditions realized when the constituent in excess of the eutectic is an intermediate constituent that crystallizes in the form of plates, stars, or polyhedral crystals. Its appearance causes a marked deviation from the structure that consists entirely of eutectic. Similarly, when the eutectoid composition in steel is departed from, films of ferrite or of Fe_3C form round the grains of pearlite and this produces a characteristic change of structure. Thus although eutectics and eutectoids are in a constitutional sense simply stages in the continuous change in constitution that accompanies the change in composition, they represent points at which discontinuous changes in structure occur. When, e.g., the carbon content of steel is increased from 0 to 1.7 per cent. the amount of ferrite decreases progressively and the amount of cementite increases progressively, but the structure does not change progressively throughout this range. It changes in a certain way up to the eutectoid point and in another way beyond it. All properties that are affected by structure, e.g. mechanical and electrical properties, may therefore be expected to exhibit some discontinuity at the eutectoid point rather than to vary progressively with the composition and constitution. In

the case of steel the tensile strength rises with the carbon content up to the eutectoid point and then begins to decrease.

The discontinuities in property-composition curves occurring at eutectics and eutectoids have been studied by Soldau (113). He found that the alloy of eutectoid composition in steel gave results that lay slightly above the lines connecting composition with hardness and electrical resistivity respectively. In alloys of tin and lead, lead and antimony, tin and zinc, &c., he likewise found that those of eutectic composition displayed a relatively greater hardness and electrical resistivity than alloys of adjacent composition. This effect of structure as distinct from constitution must always be kept in mind in considering the properties of alloys containing more than one constituent.

In pearlite and in many eutectics the decreased resistance to deformation resulting from the breaking up of the brittle constituent is counter-balanced by the increased resistance to deformation resulting from strain-hardening of the plastic constituent. In the case of eutectics in which the plastic constituent does not strain-harden appreciably the breaking up of the brittle constituent is accompanied by a decrease in the resistance to deformation of the alloy as a whole. In such alloys deformation is accompanied by a decrease in resistance to it, in other words, they are softened rather than hardened by work. The lead-antimony eutectic, and alloys consisting of skeleton crystals of lead surrounded by this eutectic, display this phenomenon of work-softening at atmospheric temperature; but practically all eutectics and eutectoids will behave in this way at sufficiently elevated temperatures (i.e. above the recrystallization temperature of the plastic constituent). This has an important bearing on the hot-working of eutectics and alloys containing them. Hargreaves (114) in a series of papers has shown that even when both constituents of a eutectic are plastic (e.g. lead and tin) work-softening occurs, and he attributes this mainly to slip between the constituents, i.e. to intercrystalline movement. As explained in Chapter IV this tends to take place to an increasing extent as the temperature is raised and only becomes marked in or above the recrystallization range. It also tends to take place to an increasing extent as the crystal size is decreased, and it probably proceeds with greater facility between crystals of different kinds than between those of the same kind. A eutectic alloy formed by metals like lead and tin has all the characteristics necessary for intercrystalline slip at atmospheric temperature. Both metals can recrystallize there and their deformation is accompanied by pronounced intercrystalline movement. In the eutectic the crystal size is small and two different kinds of crystals are present.

Alloys consisting of Two Constituents.

It now remains to discuss the general structures of alloys other than those that consist entirely of a primary solid solution, an intermediate

constituent, a eutectic, a eutectoid, or have a structure of the special type described in the next section. The most commonly occurring of these is that which consists of primary skeleton crystals of a solid solution in a matrix of eutectic. In such structures the relative amounts of skeleton crystals and eutectic may vary between wide limits. The amount of the added element soluble in the basis metal may vary from zero up to a considerable proportion, and as explained in Chapter V, when the amount of liquid that reaches the eutectic composition is small the second constituent may exist in the free state instead of in a eutectic.

The most simple example of the type of structure under consideration occurs when the added element is practically insoluble in the basis metal and the second constituent occurs in a free state. This type of structure is formed in the alloys of copper with bismuth. The solid solubility of bismuth in copper is less than 0.002 per cent., and the eutectic point lies very close to pure bismuth. In alloys containing small proportions of bismuth the small amount of copper in the eutectic liquid is deposited on the existing copper crystals leaving thin films of bismuth surrounding them. The structure is such that it does not require much bismuth for this to become the continuous constituent, and as this metal is brittle, relatively small amounts have a pronounced effect on the mechanical properties. The actual proportion of bismuth required to make copper brittle depends on the size of the copper crystals, for a quantity that is sufficient to form practically continuous envelopes round large crystals will not be capable of forming equally continuous envelopes round small ones. Thus it has been found that in coarse-grained copper as little as 0.002 per cent. of bismuth causes the metal to crack when it is cold rolled, while with fine-grained copper a certain amount of cold-rolling can be done up to a bismuth content of 0.05 per cent. Above this, however, the metal cracks as soon as it enters the rolls, and in view of the fact that copper free from bismuth can be cold rolled to a reduction in thickness of over 90 per cent. without cracking, the above is a striking example of the effect of a brittle constituent distributed in this way. Similar results are obtained with bismuth in gold, and with sulphur in nickel and its alloys. In this latter case the constituent that produces brittleness by forming more or less complete envelopes round ductile crystals is Ni_3S_2 . When manganese is absent a similar type of brittleness, most noticeable at forging temperatures, is produced in iron by small amounts of sulphur which gives rise to the formation of weak films of FeS . Finally, gold is rendered brittle by as little as 0.01 per cent. of lead which is practically insoluble in gold and forms films of a brittle constituent Au_5Pb .

The results obtained are quite different when the constituent that occurs at the crystal boundaries is ductile or forms globules instead of films. The solid solubility of oxygen in copper is less than 0.007 per cent. at atmospheric temperature, so that the presence of very small

amounts of this element gives rise to the appearance of cuprous-oxide (Cu_2O). When sufficient oxygen is present the Cu_2O occurs in a eutectic with copper, but smaller amounts appear as globules at the boundaries of the copper crystals. In any case, whether it occurs as globules at crystal boundaries or as globules or short rods in a eutectic, the brittle Cu_2O exhibits little tendency to become a continuous constituent. Consequently, it does not have a marked effect on the properties. The eutectic point is at 0.375 per cent. of oxygen (i.e. 3.4 per cent. of Cu_2O), so that even an alloy of eutectic composition does not contain much Cu_2O , and between 0.015 and 0.36 per cent. of oxygen the mechanical properties vary as follows; tensile strength increases from 14.45 to 16.61 tons per sq. in., elongation decreases from 58.4 to 34.2 per cent., and reduction in area decreases from 74.6 to 38.2 per cent. The effect of oxygen in copper is more fully discussed in Chapter XV. Lead resembles Cu_2O in that it occurs as globules, and being itself ductile has little effect on mechanical properties.

Elements that do not enter into solid solution have little effect on electrical resistivity. Thus, whereas 0.04 per cent. of phosphorus (which is soluble) decreases the conductivity of copper by 20 per cent., the effect of oxygen up to 0.06 per cent. is practically negligible, and even 0.16 per cent. only reduces the conductivity by 2 per cent. The effect of bismuth is also small so long as the envelopes formed by this metal are not continuous. With about 0.2–0.5 per cent. of bismuth, however, the envelopes become definitely continuous and a marked decrease in conductivity occurs.

When the primary crystals are those of a solid solution the conditions described above are only altered in so far as the properties of a solid solution differ from those of a pure metal. When, however, the second constituent occurs in a eutectic instead of as isolated films or globules, the arrangement of the two constituents in the eutectic has to be taken into account in addition to the arrangement of primary skeletons and eutectic. As before, the most pronounced effects of the structure are revealed when the solid solution is ductile and the second constituent of the eutectic brittle. This condition is of frequent occurrence in industrial alloys. Iron-carbon alloys containing up to 1.7 per cent. of carbon solidify as solid solutions of carbon in iron, and when this carbon content is exceeded a eutectic appears and forms a matrix in which the skeleton crystals of solid solution are embedded. In pure iron-carbon alloys this eutectic consists of the solid solution austenite and Fe_3C , but the presence of silicon causes the carbon to appear as graphite instead of Fe_3C . These factors lead to a differentiation of the three main types of alloys based on iron. Those that solidify as solid solutions are the steels, those that contain the austenite-cementite eutectic are the white cast irons, while those that contain the austenite-graphite eutectic are the grey cast irons. As the grey irons invariably contain substantial amounts of silicon there are actually only two types of pure

iron-carbon alloys, and of these the steels can be hot-worked with comparative ease while the white irons, on account of the cementite in the eutectic, can only be worked with the greatest care when the carbon is below 2.5 per cent. and not at all when it is higher. Although alloys containing between 1.7 and 2.5 per cent. of carbon may be hot-worked if great care is exercised in the initial stages so that the Fe_3C will be broken up without fracturing the alloy, such alloys are used commercially only in the cast condition. High-speed steel, however, has a structure similar to white cast iron and is always subjected to a considerable amount of working. This alloy contains about 0.7 per cent. of carbon, 18 per cent. of tungsten, and substantial amounts of other elements as described in Chapter XIII. It solidifies as primary skeleton crystals of austenite in a matrix of a eutectic of austenite and a double carbide $\text{Fe}_4\text{W}_2\text{C}$. This carbide is very hard and is brittle at forging temperatures. Cast ingots are very tender and must be carefully handled. After solidification they are annealed for 24 hours at 800–850° C., then carefully heated to the forging temperature and carefully worked under the hammer. This working destroys the continuity of the carbide and establishes the continuity of the austenite. By means of forging and repeated reheating the structure is eventually converted into one consisting of globules of carbide in a matrix of austenite and may then be worked to any required extent.

In the alloys of aluminium and copper a eutectic containing CuAl_2 appears when the limit of solubility of copper in aluminium is exceeded. Under equilibrium conditions this occurs at 5.65 per cent. of copper, but in practice the eutectic appears in cast alloys of considerably lower copper content. It contains 33 per cent. of copper, and under experimental conditions alloys containing up to 10 per cent. of copper have been hot-worked. In industrial alloys intended for forging the copper content is, however, kept at 5 per cent. or under and those containing 8 and 12 per cent. are used only in the cast condition. The strength in this condition rises rapidly with the copper content up to 6 per cent. and then more slowly up to 12 per cent. The elongation falls from 20 per cent. in cast commercially pure aluminium to 1 per cent. in an alloy containing 12 per cent. of copper. Above 14 per cent. the tensile strength begins to decrease with rising copper content as a result of the brittleness of the alloy, but the hardness increases up to 54 per cent. of copper (CuAl_2). In the alloys of aluminium and silicon quite different results are realized. In these the limit of solid solubility is 1.65 per cent. silicon and the eutectic which consists of aluminium and silicon contains 11.6 per cent. of the latter. Alloys containing up to 13 per cent. of silicon can be rolled or extruded when hot, and as the silicon content is increased from 2 to 14.5 per cent. the tensile strength in the chill cast condition increases from 8 to 14 tons per sq. in., while the elongation decreases from 10 to 4 per cent. The rather exceptional behaviour of these alloys is due to the greater plasticity of silicon as compared with

Fe_3C , CuAl_2 , and other hard intermediate constituents, and to the fact that in chill cast or modified alloys the particles of silicon are small and globular.

The conditions realized in alloys that consist of a pure metal or primary solid solution plus a eutectoid are in general similar to those described above, but in considering them it is necessary to take account of the specific properties of the eutectoid and its distribution in the alloy. Steels containing less than 0.9 per cent. of carbon consist of ferrite (comparatively pure α -iron) and pearlite, but owing to the fact that these constituents result from the decomposition of a solid solution (austenite) their arrangement is different from that of primary crystals in a matrix of eutectic. It varies with the carbon content, the rate of cooling through the range in which the austenite decomposes, and the grain size of the austenite, but in general, so far as slowly cooled steels are concerned, those containing less than 0.45 per cent. of carbon consist of grains of pearlite distributed throughout the ferrite, those containing more than 0.7 per cent. consist of grains of pearlite surrounded by envelopes of ferrite, and those of intermediate composition have a transitional structure. As the pearlite is not the continuous constituent in the steel, and as the cementite is not continuous in the pearlite, all steels up to 0.9 per cent. of carbon are capable of being cold-worked to a considerable extent unless the plates of cementite are thick, in which case steels near the eutectoid composition cannot be cold-worked. The arrangement of the constituents is such that the cementite stiffens the metal without dominating its properties in the way that bismuth dominates those of copper or CuAl_2 those of copper-aluminium alloys containing more than 6 per cent. of copper. Between 0 and 0.9 per cent. of carbon the strength increases from 16–19 to 48–62 tons per sq. in., while the elongation decreases from 50–70 to 4–13 per cent.

Other examples of alloys in which eutectoids occur are provided by those of copper with aluminium and tin respectively. Both of these consist of α and δ . The copper-aluminium eutectoid contains 11.9 per cent. of aluminium and has a Brinell hardness of about 250, while that of copper-tin contains 27 per cent. of tin and has a Brinell hardness of about 260. Under equilibrium conditions the eutectoid in copper-aluminium alloys appears at an aluminium content of 9.8 per cent., but in practice it is found in cast alloys containing above 7 per cent. Its appearance is accompanied by a pronounced decrease in elongation as shown in Fig. 545, but the tensile strength continues to rise until the eutectoid composition is reached, when it falls rapidly in consequence of the appearance of free δ . The aluminium content of alloys intended for working is kept at 7 per cent. or under. Alloys of higher aluminium content are used in the cast condition and are frequently cooled at a rate that prevents the change from β to the α - δ eutectoid. Under equilibrium conditions the eutectoid in copper-tin alloys appears at 14

per cent. of tin, but in practice it is found in cast alloys containing more than 7 per cent. It causes a pronounced decrease in elongation as shown in Fig. 544, but the strength continues to rise up to 16 per cent. of tin, above which the alloys become definitely brittle. Industrial alloys intended for working contain 5 per cent. of tin or less. Others containing from 10 to 14 per cent. are used in the cast condition for purposes in which the presence of the hard δ -constituent is an advantage. Higher proportions of tin (15–30 per cent.) are used in bell metal.

It remains to discuss the structures resulting from changes in solid solubility, and attention will be confined to alloys that solidify as a solid solution. In alloys that contain a eutectic at solidification the excess constituent deposited from solid solution may be precipitated either on the crystals already existing in the eutectic, in which case it has no appreciable effect on the structure or properties, or at the boundaries or within the crystals of the basic constituent, in which case its effect is the same as in the absence of eutectic. In alloys that solidify as a solid solution little or none of the excess constituent is deposited from solution at temperatures close to that of solidification, so that whatever effect the precipitation of this constituent may have on mechanical properties it is always possible to hot-work them as required. Alloys of this type may therefore be used in the cast or hot-worked condition and their structure and properties vary considerably with their condition.

In cast alloys the excess constituent precipitated during cooling may under suitable conditions separate at the boundaries of the solid solution crystals. This result is favoured by slow cooling, but it is also influenced by the size of the crystals and the nature of the alloy concerned. When separation does take place at the boundaries the effect on the properties depends on the amount of the excess constituent, its properties, and the extent to which it isolates the solid solution grains from each other. The maximum amount of excess constituent that can form is determined by the difference between the solid solubility at the eutectic temperature and that at atmospheric temperature. The amount that actually forms is invariably less than this, for equilibrium conditions are never realized in ordinary practice. In any case the amount of the excess constituent formed is usually small and does not have a pronounced effect on the properties unless it is brittle and tends to form continuous envelopes. In iron-carbon alloys containing between 0.9 and 1.7 per cent. of carbon Fe_3C is precipitated at the austenite grain boundaries during slow cooling from 1,130 to 700° C. This carbide exhibits a strong tendency to form such envelopes so that when the residual austenite changes to pearlite the structure consists of grains of pearlite surrounded by envelopes of cementite. Thus above 0.9 per cent. of carbon the tensile strength begins to decrease with increasing carbon content, i.e. definite brittleness appears. The results are quite different in the alloys of aluminium and copper, for in this case, the mechanical properties are similar in alloys that are slowly cooled and

those that are quenched so as to prevent the precipitation of CuAl_2 . In this case the CuAl_2 deposited during slow cooling does not effectively isolate the aluminium grains.

When the rate of cooling of cast alloys of the type under discussion is increased, the excess constituent tends to an increasing extent to precipitate in the form of plates and needles along the crystallographic planes of the basic solid solution. When these are brittle and large they tend to produce brittleness by facilitating fracture through the crystals, but they are not so effective as boundary envelopes because they have not the same degree of continuity. As the rate of cooling is increased the plates become smaller and smaller and are increasingly effective in stiffening the alloy without producing brittleness. This increase in the rate of cooling is accompanied, however, by a decrease in the amount of the excess constituent precipitated and the conditions just mentioned merge gradually into those described in the next section.

If alloys of the type described above are forged in the range in which the hard constituent is precipitating, the working has a pronounced effect on its distribution. In the first place, the grains of the basic solid solution are continually being deformed and recrystallized, and there is no fixed system of boundaries or crystallographic planes along which precipitation can occur. Secondly, any plates or films of appreciable size are broken up by deformation, and thirdly, whatever the shape of the small particles formed they are converted into globules by surface tension. Thus, when steel containing more than 0.9 per cent. of carbon is forged as it cools through the range of formation of Fe_3C this constituent occurs in the final structure as globules rather than as plates or boundary films. In such a condition it hardens the steel and increases its resistance to wear without promoting definite brittleness. This is the structure sought in carbon steel tools. As far as the form of the carbide is concerned it is similar to that of high-speed steel and other forged alloys in which a hard constituent is present.

HEAT TREATMENT

A considerable amount of metal goes into use just as it is cast, but for most applications some heat and mechanical treatment are necessary. The heat treatments may be divided into two classes. In the first are included those that are primarily intended to raise the metals to temperatures suitable for hot-working, to relieve internal stress, or to eliminate the effects of cold-working. These are considered in Part IV. In the second are included those that are primarily intended to modify the structure and constitution of the metal by controlling the conditions under which changes in the solid state occur. The purpose of this section is to describe the general principles of operations of this kind. It is evident that if an alloy that undergoes changes in the solid state is heated for working, to relieve internal stress or to eliminate the effects

of cold-working, its constitution and structure may be modified at the same time; and if it is heated and cooled under controlled conditions for this latter purpose the effects of previous cold-working may be eliminated and internal stress may be relieved or produced according to the rate of cooling. The two types of heat treatment are thus closely related and this aspect is considered in connexion with specific alloys in Parts V and VI. Any heating and cooling operation to which solid metal is subjected may be called a heat treatment, and sometimes the term is thus used to apply to operations of both classes. More usually, however, it is used to apply specifically to treatments of the second class and it is in this sense that it will be employed in this section.

Changes in the solid state are affected by time, and if an alloy undergoes such changes, its constitution and structure at atmospheric temperature will depend on the way in which it is cooled. Heat-treating operations of the type under consideration are essentially methods of obtaining a desired constitution and structure by controlling the rate of cooling. This may be accomplished by controlling the cooling of the alloy after casting, and in practice this is sometimes done, but more generally the desired result is obtained by subjecting the alloy to one or more heating and cooling cycles after it has cooled to atmospheric temperature as a cast or wrought article. The treatment begins with the alloy in a certain condition. It is then heated and cooled and obtained in a different state which may either be nearer to or farther from equilibrium than the original one. If the former is the case the operation is usually described as annealing. This term is also used to denote treatments performed to relieve internal stress or to eliminate the effects of cold-working, and the justification of its varied use depends on the fact that in each case the metal is brought nearer to a condition of equilibrium than it was before. In so far as it is applied to heat treatments of the second class, annealing consists of heating above the temperature range in which the changes in the solid occur, and then cooling slowly to enable a condition approaching equilibrium to be realized. As the equilibrium condition in different types of alloys has already been described, and as the effects of annealing on specific alloys are discussed in Parts V and VI, this type of treatment need not be dealt with here. Attention will be directed to those treatments that are designed to obtain conditions more remote from equilibrium than those existing in the alloy before the treatment begins. Subsequent treatments may then be used to allow the alloy to proceed to a greater or less extent towards its equilibrium condition.

In heat treatments of this type the first requirement is that the alloy must undergo changes in the solid state so that its equilibrium condition at atmospheric temperature is different from that at some higher temperature. The second requirement is that the alloy must be heated to such a temperature and for such a time that the changes that take place during heating proceed to the necessary extent. The third

requirement is that it must be cooled at a rate that prevents the changes during cooling taking place in the normal way. Unless special precautions are taken the alloy will not be in a condition of equilibrium at atmospheric temperature when the treatment begins, but in general it is sufficiently near it to be considered as such for the present purpose. In any case the first stage in the treatment is to heat the alloy, and at the higher temperature a new condition of equilibrium is established. At this temperature equilibrium is reached more rapidly, and for the time being it may be supposed always to be realized, leaving the effects of failure to reach equilibrium at the higher temperature to be dealt with in Parts V and VI. Under these conditions discussion of the general principles of heat treatments of this class is reduced to a consideration of the influence of accelerated cooling on changes in the solid state.

As a rule, variations in cooling mean variations in the rate at which the alloy is cooled from the appropriate high temperature down to near atmospheric temperature, but other variations are possible. Thus it may be cooled at a certain rate down to some temperature above atmospheric and (1) maintained there for any required length of time, (2) cooled more slowly, or (3) more rapidly than before. Furthermore, it may be cooled at a certain rate to a temperature below atmospheric and (1) maintained there for any required time, or (2) allowed to return to atmospheric temperature. From a strictly scientific point of view atmospheric temperature has no special significance, but from a practical point of view it has, and this applies to experiments as well as to industrial operations. Thus, although the behaviour of an alloy that is cooled to atmospheric temperature and retained there may not have any more fundamental importance than its behaviour when cooled to 200° C. and retained there, it is necessary in practice to recognize a great difference between these two treatments.

In practice, variations in the rate of cooling cannot be considered apart from the methods available for cooling and the size of the pieces to be cooled. Slow rates of cooling may be obtained by cooling in furnaces over any required period of time, but rapid rates are more difficult to arrange for. What is usually regarded as normal cooling is obtained when the articles are withdrawn from the heating furnace and allowed to cool freely in air. Under these conditions the rate of cooling varies with the size of the piece, and the rate at any point in a given piece varies with its distance from the surface. When slower rates are employed, as when the metal is cooled in a furnace by stopping or reducing the supply of heat or gradually moving the pieces into cooler zones, the effect of size becomes less marked, i.e. small and large stock can be made to cool at similar rates and the difference in the rates at the surface and centre of the larger pieces can be reduced to a minimum. When, however, faster rates are obtained by using an air blast, a water-spray, immersing in molten metal or salts of low melting-point, or by

quenching in water or oil, the influence of size becomes more marked, i.e. the rate of cooling decreases, and the difference in the rates at the surface and centre increases as the size of the piece increases. These aspects of cooling are dealt with more fully in Part V, but in order not to introduce too many complications into this section attention will be confined mainly to the results obtained with pieces that are small enough to be immune from the effect of size.

Changes of all the types described in this chapter are affected by the rate of cooling, viz. polymorphic changes, diffusion changes, changes in solubility and from one constituent to another, eutectoid changes, and disorder to order changes. Each type of change is affected in a particular way, but the extent to which it can be modified by varying the rate of cooling within available limits varies from alloy to alloy. In order to describe in detail the effects of accelerated cooling it is necessary to deal with specific types of alloys, but in order to show the relations between all alloys of suitable types a brief general description may be given here.

We may take as our starting-point the rate of cooling which permits equilibrium conditions to be realized during the changes in the solid state. Under these conditions the phase stable at the high temperature begins to change at a certain temperature to the phase or phases stable at the lower temperature and this change continues to completion or until atmospheric temperature is reached. Thus in pure iron the $\gamma \rightarrow \alpha$ change takes place at 906°C. , and in iron-carbon and copper-aluminium alloys the eutectoid changes take place at 725° and 537°C. respectively. In iron-carbon alloys containing less than 0.9 per cent. of carbon the change from austenite to ferrite takes place over a range that varies with the carbon content, while in aluminium-copper alloys the precipitation of CuAl_2 is (theoretically) still proceeding when atmospheric temperature is reached. When the equilibrium rate of cooling is exceeded, the temperatures at which the changes begin are lowered, but, as explained in the section dealing with 'The Effect of Time and Temperature on Changes in Solid Solubility', they still take place to a considerable extent because the formation of smaller crystals enables them to proceed more rapidly. Thus the first effect of increasing the rate at which steels containing less than 0.9 per cent. of carbon are cooled from the austenitic range is to produce smaller crystals of ferrite and finer pearlite. Similarly, the first effect of increasing the rate of cooling of a 4 per cent. aluminium-copper alloy is to obtain the CuAl_2 in a finer state of division. In the case of pure iron the only result that can be obtained by increasing the rate of cooling to the maximum extent is to refine the α -iron crystals and alter their shape.

But there is a limit to the extent to which the rate of a change may increase by the formation of smaller crystals of the phases stable at lower temperature. Thus, when the rate of cooling is progressively increased from the equilibrium rate, the first effect is to lower the change and cause it to take place more rapidly by the formation of

smaller crystals, while the subsequent effect is to lower the change further and cause it to take place more slowly because of the lower temperature. Consequently when the rate of cooling exceeds a certain limit each further increase results in a decrease in the rate of change. It therefore proceeds to a less extent and when cooling is sufficiently rapid it is completely suppressed. This suppression involves cooling at a certain 'critical rate' down to a certain temperature, and what happens after this is reached depends on whether the original rate of cooling is maintained or not, and whether any other type of change takes place. If the original rate of cooling is maintained, the phase stable at high temperature may be retained at atmospheric temperature. In pure iron-carbon alloys austenite cannot be retained entirely at atmospheric temperature, but the addition of sufficient amounts of manganese, nickel, or nickel and chromium enables this to be done. In aluminium-copper alloys containing between 0.5 and 5.65 per cent. copper the formation of CuAl_2 can be prevented by rapid cooling and the alloys retained at atmospheric temperature as solid solutions of copper in aluminium. Similarly, in numerous other alloys, and notably in copper-beryllium, copper-nickel-silicon and copper-nickel-aluminium alloys, changes in solid solubility can be prevented by rapid cooling. If, however, the original rate of cooling is not maintained, and cooling is stopped or continued at a slower rate after the changes have been suppressed, then these may take place slowly at the temperature at which cooling is stopped or retarded. Furthermore, in certain alloys, when the normal changes are suppressed others take place even when the original rate of cooling is maintained, and this prevents the retention of the high-temperature phase down to atmospheric temperature. The best known example of this occurs in steel, in which, when the decomposition of austenite into ferrite and cementite is prevented, the iron changes from the γ - to the α -form with the carbon still in solution, thus producing the constituent 'martensite' which is a solid solution of carbon in α -iron. Similar changes occur in copper-aluminium and copper-tin alloys.

When the normal changes are suppressed by rapid cooling, an alloy consists at atmospheric temperature of the phase stable at high temperature or of some other phase that is formed because of the conditions realized during rapid cooling. In neither case is the phase retained stable at atmospheric temperature. It may, however, persist indefinitely or decompose either slowly or rapidly. Austenite retained by rapid cooling and the addition of suitable quantities of manganese, nickel, chromium, &c., persists indefinitely unless it is deformed, and the same applies to the solid solutions obtained by the rapid cooling of copper-beryllium, copper-nickel-silicon, and copper-nickel-aluminium alloys. Martensite (a solid solution of carbon in α -iron) when freshly retained by rapid cooling undergoes a certain amount of decomposition (i.e. precipitation of Fe_3C), but the amount of this is small and it pro-

ceeds at a diminishing rate so that a persistent state is soon reached. The solid solution obtained by the rapid cooling of aluminium-copper alloys is not persistent, however, at atmospheric temperature, and it decomposes at an appreciable rate with the 'precipitation' of CuAl_2 .

Phases that are not stable at atmospheric temperature become increasingly unstable when heated. Thus austenite, martensite, and other constituents that are completely or substantially persistent at atmospheric temperature tend to decompose on heating. The relations between time, temperature, and rate of decomposition depend, however, on the composition of these constituents, and while martensite in a straight carbon steel begins to decompose at an appreciable rate when heated to 100°C ., austenite containing sufficient nickel and chromium may be heated to any required temperature without decomposing, i.e. the range of persistence is co-extensive with the range of stability as described in Chapter XII.

In practice, heat treatments of the type under consideration are used when cooling under controlled conditions leads to retention of the alloy in a condition which displays special properties or from which special properties can be obtained by a subsequent treatment. Most of the effects mentioned above are utilized in this way. Thus steel may be cooled at accelerated rates to secure a finer ferrite-pearlite structure and a more finely laminated pearlite without suppressing those changes. Steels, aluminium-copper, and several other alloys may be cooled so as to obtain at atmospheric temperature the phases stable at high temperature, and steels may also be cooled so as to obtain the constituent martensite which is formed only during rapid cooling. Heat treatments of this kind are closely associated with variations in composition which are utilized to supplement the effect of the rate of cooling. A number of elements, e.g., have the same effect on steel as acceleration of the rate of cooling, and nickel, manganese, chromium, and molybdenum are added to decrease the rate of cooling required to obtain martensite or to enable unaltered austenite to be retained at atmospheric temperature. When all the possible effects of variations in composition and rate of cooling are taken into account heat treatment becomes a very wide subject, but its essential features can be illustrated by considering certain aspects of the heat treatment of steel and aluminium-copper alloys.

The Heat Treatment of Steel.

The changes that normally occur in solid iron-carbon alloys are represented by Fig. 168. In the area above the line *GSE* the stable phase is austenite (i.e. a solid solution of carbon in γ -iron). In alloys containing less than 0.87 per cent. of carbon the austenite begins to decompose when cooled to the appropriate point on *GS*. Ferrite, which in a straight iron-carbon alloy is practically pure α -iron, begins to form and continues to do so while the temperature falls until the remaining

austenite reaches the point *S*. At this point the decomposition of the austenite is completed by the simultaneous formation of ferrite and Fe_3C , which gives pearlite. In alloys containing more than 0.87 per cent. of carbon the decomposition of the austenite begins at the appropriate point on *ES*. Fe_3C is formed as the temperature falls until the austenite reaches *S* when its decomposition is completed by the formation of pearlite. Thus steels containing less than 0.87 per cent. of carbon consist below 725°C . of ferrite and pearlite while those containing more than 0.87 per cent. consist of Fe_3C and pearlite.

The grain size of the austenite existing above the line *GSE* is influenced by the temperature to which the steel is heated and also by its previous treatment, and this has a pronounced effect on the results obtained with varying rate of cooling. This is discussed in Chapter XI. Apart from this, every change in the rate of cooling through the range in which the transformations occur affects the condition of the steel at atmospheric temperature. Beginning with the equilibrium rate it may be said that the first effect of increasing the rate of cooling is to (1) lower the temperature at which the changes occur, (2) increase the fineness of the pearlite lamella, (3) increase the fineness of the ferrite-pearlite or cementite-pearlite structure, and (4) increase the amount of pearlite relative to that of ferrite or cementite in steels not of eutectoid composition. All these effects are utilized in practice and are obtained by increasing the rate of cooling or adding other elements, but at present we are mainly concerned with the consequence of greater increases in the rate of cooling. These have the effect of first partially and then completely suppressing the changes described above so that austenite is retained unaltered at temperatures considerably below the line *PK* (Fig. 168).

Suppression of the normal changes means that the rate of cooling is sufficient to lower them to a range in which they take place more slowly than at higher temperature, and if no other changes could take place maintenance of the original rate of cooling should result in the retention of austenite at atmospheric temperature. As this constituent is cooled further below the range in which it is stable it becomes increasingly unstable, but is prevented from decomposing in the normal way because the changes concerned involve diffusion and therefore depend on time. During rapid cooling they are prevented from taking place, but another change that does not depend on time occurs. This involves no diffusion and consists simply of a change in the arrangement of the iron atoms, viz. from that characteristic of γ -iron to that characteristic of α -iron with the carbon still in solution. Thus a solid solution of carbon in α -iron is obtained and is known as martensite.

The above effects of the rate of cooling apply to steels containing appreciable amounts of carbon. The effect on pure iron is quite different, and the same may be said of alloys of low carbon content which serve as the connecting link between pure iron and alloys containing more than

about 0.15 per cent. of carbon. As explained at the beginning of this chapter the $\gamma \rightarrow \alpha$ change in pure iron can be lowered by accelerating the rate of cooling and this influences the structure of the α -iron. The change from austenite to martensite is simply this change taking place in the presence of carbon and without rejection of carbon from the α -lattice. It is thus continuous with the $\gamma \rightarrow \alpha$ change in pure iron. The higher the carbon content of the austenite the lower is the temperature at which the change from γ to α begins. This is indicated for slow cooling by line *GS* (Fig. 168) and for rapid cooling by line *AM* in Fig. 181. This latter shows the temperatures at which austenite begins to change to martensite in rapidly cooled steels of different carbon content. In pure iron the effect of increasing the rate of cooling is continuous, i.e. there is no sudden change from one condition to another at a particular rate of cooling. In steels, however, there is a more or less sudden change from the ferrite-pearlite structures formed during slow cooling to the martensite formed during rapid cooling. When the carbon content is low, however, the behaviour of steel is intermediate between that characteristic of steels of higher carbon content and that characteristic of pure iron. This behaviour is considered in Chapter XI. For the present we are dealing only with those alloys in which rates slower than a certain maximum permit the formation of the normal constituents, while rates faster than a certain minimum suppress the normal changes and retain martensite. Intermediate rates permit a certain amount of austenite to change to pearlite and retain the remainder as martensite.

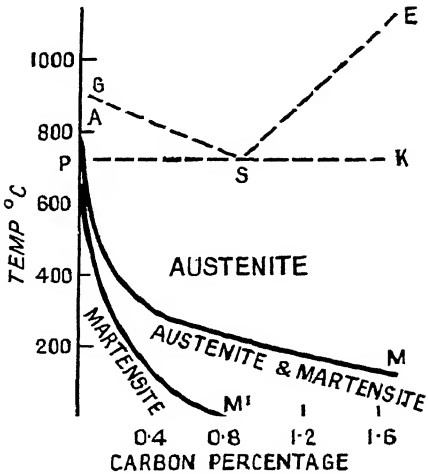


FIG. 181.

If austenite is cooled down to about 500° C. at a rate that prevents any changes taking place, maintenance of this rate of cooling will prevent any transformation above the line *AM* (Fig. 181). It may even be somewhat reduced without any change taking place, but if it is sufficiently reduced, decomposition of the austenite will begin as described in Chapter XI. When undecomposed austenite reaches the appropriate point on the line *AM*, the lattice of the iron begins to change from the face-centred to the body-centred form with the carbon still in solution. This transformation is not affected to an appreciable extent by time but only by temperature. Thus, as cooling continues the change proceeds and when cooling stops the formation of martensite stops. The amount of martensite formed during cooling through a certain range of

temperature is to a large extent independent of the rate of cooling through this range, but the effect of varying the rate of cooling through the range of formation of martensite is complicated by the decomposition of the martensite. The line AM' in Fig. 181 indicates the temperatures at which the austenite-martensite change is substantially completed in steels of different carbon content. This line passes below atmospheric temperature at about 0.9 per cent. of carbon. In steels containing more than this amount some austenite remains when atmospheric temperature is reached and the amount increases with the carbon content. As the formation of martensite is affected by temperature and not by time, it continues to form when steels containing more than 0.9 per cent. of carbon are cooled below atmospheric temperature, but the austenite retained by rapid cooling persists without change so long as the steel is kept at atmospheric temperature. It should be noted that the lines AM and AM' in Fig. 181 have no significance other than that they indicate the temperatures at which the austenite-martensite change begins and ends in steels of different carbon content, i.e. the line AM' does not show the composition of the martensite formed, nor does the austenite alter in composition along the line AM while the transformation is proceeding.

Under equilibrium conditions austenite of any given composition begins to decompose at the appropriate point on the line GSE , but when the cooling is sufficiently rapid it may be retained undecomposed down to the line AM . It then begins to change to martensite, and as this transformation is not appreciably affected by time it cannot be lowered, interrupted, or suppressed, by the most rapid rates of cooling. Below GSE austenite is unstable, i.e. it tends to decompose at a rate that depends on the temperature. Between GSE and about 550°C . the rate of decomposition increases as the temperature falls, but below 550°C . the rate of decomposition decreases as the temperature falls except when martensite is being formed. As shown in Chapter XI the rate of decomposition of austenite into ferrite and cementite is comparatively slow in steels containing more than 0.5 per cent. of carbon at temperatures just above AM . At constant temperatures below AM the rate of decomposition of austenite becomes still slower (martensite is not formed at constant temperature but only during continuous cooling), and at atmospheric temperature this rate is so slow that austenite is for all practical purposes persistent. Martensite is unstable at all temperatures and its decomposition into ferrite and cementite is simply a question of time, temperature, and carbon content, e.g. the rate of decomposition increases with the temperature and the carbon content. At atmospheric temperature martensite of high carbon content can decompose to a small extent, but in general it may be said to be persistent at this temperature. At temperatures above 100°C . it decomposes at an appreciable rate while above 200°C . its decomposition is rapid. In steels that contain less than 0.9 per cent. of carbon the

temperature at which the formation of martensite begins is high enough to permit some decomposition to take place before atmospheric temperature is reached. In steels that contain more than 0.9 per cent. of carbon some austenite is retained by rapid cooling. Consequently, it appears practically impossible to obtain a specimen consisting entirely of undecomposed martensite.

Martensite results from the $\gamma \rightarrow \alpha$ lattice change taking place with carbon still in solution, but owing to the presence of carbon the lattice cannot change completely to the body-centred form. Thus the iron is retained in a condition intermediate between the face-centred and body-centred cubic, i.e. in the tetragonal form, as explained at the beginning of this chapter. The deviation from the body-centred lattice increases with the carbon content of the martensite, and as this increases from 0 to 1.4 per cent. two sides of the unit cell decrease from 2.861 Å. to 2.840 Å., while the third side increases from 2.861 Å. to 3.034 Å. The transformation from austenite to martensite takes place along the (111) planes in the austenite and thus a particular type of Widmanstätten structure known as the martensitic structure is produced. Examples of this structure are shown in Fig. 164, which shows martensite in a 0.1 per cent. carbon steel quenched in water, and in Fig. 165, which shows martensite needles in a matrix of austenite in a 1.7 per cent. carbon steel quenched in water. Further examples of this structure are described in Chapter XI.

When martensite is heated it begins to decompose at an appreciable rate at temperatures above 100° C., and during continuous heating this decomposition reaches its maximum at about 260° C. and is completed at about 300° C. During this change the carbon comes out of solution in the α -iron and forms crystals of cementite. These cannot be seen under the microscope, for they are of sub-microscopic dimensions, but from analogy with similar changes it may be inferred that they consist of minute plates formed along the crystallographic plates in the α -iron crystals. The steel then consists of small α -iron crystals arranged like interlaced needles or plates with cementite films in their crystallographic planes. On further heating the cementite plates change into globules under the influence of surface tension, and at the same time coalescence takes place. This process is of great importance in connexion with the heating of solid solutions retained by rapid cooling. As the term implies, small globules combine to form larger ones, but this does not actually take place by the globules moving towards each other and then uniting. What really happens is that some globules dissolve, i.e. carbon goes into solution and is redeposited as cementite on other globules. Thus by a process of solution and redeposition some globules grow at the expense of others and the result is the same as if they had actually coalesced. While spheroidization and coalescence of the cementite is going on, growth of the α -iron crystals is taking place, and when martensite is heated to above 600° C., cooled, and microscopically

examined, the crystals of α -iron and the globules of cementite can be observed. The deposition of carbon from solution in α -iron is a change which definitely ends when the carbon content falls to the amount normally soluble (0.01–0.03 per cent.), but the other changes go on continuously as a function of time and temperature unless the steel is heated above the line *PSK* (Fig. 181) when austenite begins to reform.

It will be evident from what has been said in this section that the constitution and structure of steel may be varied within wide limits by different heating and cooling cycles. This aspect is fully considered in Part V. Special interest attaches, however, to thermal treatments which involve cooling from the austenite range at a rate that leads to the formation of martensite. This constituent is distinguished by its great hardness and its high remanent magnetism and coercive force. Furthermore, by heating martensite at temperatures between 150° C. and 650° C. the hardness may be reduced to any required extent and the structures which result display a better combination of hardness, strength, and toughness than those obtainable in other ways. Steels for use as permanent magnets are cooled so as to obtain martensite and are not subsequently heated above 100° C., because the partial decomposition that then takes place lowers their remanent magnetism and coercive force. For most other applications the martensite is heated to reduce its hardness and brittleness. The heating temperature varies from 150° to 250° C. in the case of tools to about 600° C. in the case of components subjected to repeated stress, e.g. motor-car axles, crankshafts, &c.

To obtain martensite in plain carbon steels it is generally necessary to cool the hot steel in cold water. This drastic process is very liable to produce cracks and has the additional disadvantage that the rate of cooling diminishes rapidly as the distance from the surface increases. Thus, while small sections may be cooled throughout at a rate that retains martensite, in sections greater than 0.75 in. diameter the necessary rate is not attained at the centre. The operation is known as quenching (with reference to the method of cooling) or hardening (with reference to the result obtained). The subsequent heating to reduce the hardness and brittleness is known as tempering. A number of elements when added to carbon steel have the effect of decreasing the rate of cooling required to suppress the normal changes and retain martensite. Of these the most important are nickel, manganese, chromium, molybdenum, and vanadium, and they are added in varying amounts and combinations to produce steels in which martensite may be obtained by cooling in oil or air instead of water. Owing to the slower rates of cooling required to harden these steels the hardening effect penetrates to greater depths and thus larger sections may be properly treated. The addition of these and other elements has other effects on the steel, but in general the most important characteristic of these alloy or

special steels is that they harden with slower cooling and to greater depths than carbon steels.

Heat Treatment of Aluminium-Copper and Similar Alloys.

The essential characteristic of the phenomena just described in connexion with steel is that when the rate of cooling is sufficient to suppress the normal changes another change takes place at a lower temperature so that the phase stable at high temperature is not retained. A similar phenomenon occurs in copper-aluminium alloys (containing 10–14 per cent. of aluminium) and also in the copper-tin alloys. In both these cases rapid cooling prevents the decomposition of β into $\alpha + \delta$, but it does not entirely inhibit the change from the body-centred lattice of β to the face-centred lattice of α . Thus, in effect, supersaturated α solid solutions are retained, which are softer than the α - δ mixtures obtained with slow cooling. Thus whereas steel is cooled rapidly to increase its hardness, copper-aluminium alloys are cooled rapidly to prevent the development of brittleness by the formation of δ , and, although in practice it is not done, a similar treatment would have the same effect on copper-tin alloys containing more than 10 per cent. of tin.

The phenomenon referred to above occurs only in the alloys mentioned, but there are numerous others in which it is possible to retain at atmospheric temperature the phase stable at high temperature. This occurs when changes in solid solubility, changes from one constituent to another, eutectoid changes or disorder-order changes, are suppressed by rapid cooling down to atmospheric temperature. In most cases of this kind a change in solid solubility is involved, and attention may accordingly be directed in the first place to the behaviour of alloys of this kind, and particularly to those of aluminium-copper and certain other alloys in which important practical advantages are obtained by treatments that involve suppressing the normal changes.

At the eutectic temperature (548°C.) copper is soluble in solid aluminium to the extent of 5.65 per cent. under equilibrium conditions (Fig. 153), but only 0.5 per cent. is soluble at atmospheric temperature. The essential feature of the treatment under consideration is to retain at atmospheric temperature the solid solution stable at high temperature, and practically important consequences arise from subsequent changes that take place in this solid solution. As the phenomena under consideration are exhibited most plainly and effectively by alloys in which all the copper may be brought into solution by heating below the eutectic temperature, attention may be confined to those containing not more than 4.5 per cent. of this metal.

Cast alloys are not in a condition of equilibrium, and thus, whereas the diagram (Fig. 153) indicates that all alloys containing less than 5.65 per cent. of copper should solidify as solid solutions, actually some eutectic (or free CuAl_2) may appear when the copper content is as low

as 2 per cent. If castings are cooled fairly rapidly the amount of copper retained in solid solution at atmospheric temperature is more than is soluble under equilibrium conditions and the phenomenon to be described presently is exhibited to some extent. It is more pronounced, however, if a greater amount of copper is retained in solid solution, and this may be obtained by heating the casting at 500–520° C. This is known as the solution heat treatment, and by means of it the copper content of the solid solution may be raised to about 4.5 per cent. The duration of this treatment depends on the amount of CuAl_2 existing in the free state in the alloy and the way in which it is distributed. As explained in an earlier section, the copper content of the solid solution in immediate contact with CuAl_2 changes during heating along the line db (Fig. 153), so that when 500° C. is reached these areas contain 4 per cent. of copper. The copper content of the solid solution diminishes, however, as the distance from the CuAl_2 particles increases, and diffusion must take place before it becomes a uniform solution containing this amount. The time required for complete diffusion increases with the distance over which it must take place, i.e. with the distance between the particles of CuAl_2 . In cast alloys the structure consists of comparatively large grains outlined by eutectic (or free CuAl_2) and a long time is required to establish a uniform concentration of copper throughout the solid solution. If, however, the cast alloy is rolled or forged, the original large crystals are broken up and the network of eutectic (or CuAl_2) outlining these is converted into more or less uniformly distributed particles of CuAl_2 . Thus complete solution is more readily brought about in worked than in cast alloys.

When all the CuAl_2 has been dissolved (or, in the case of alloys containing more than 4.5 per cent. of copper, when the copper content of the solid solution has been raised to this figure), the alloy must be cooled so as to retain this copper in solid solution. This is usually accomplished by quenching in cold water, but for many purposes slower rates of cooling are sufficiently effective. When the solid solution is retained unaltered at atmospheric temperature its mechanical properties are better than those of the slowly cooled alloy, and the advantage of this treatment is greater in the case of cast than of worked alloys. The point of particular interest, however, is that, after quenching, a change takes place in the solid solution and leads to a gradual increase of strength and hardness. This is known as age-hardening, and it is because of the improvement in mechanical properties obtainable in this way that the treatment under consideration is of great importance. Maintaining an alloy at atmospheric temperature while it undergoes a change is not exactly a treatment, but it is frequently convenient to refer to it as such and it is called ageing.

The phenomenon of age-hardening arises from the fact that the solid solution retained by quenching is not persistent at atmospheric temperature and therefore tends to undergo a change which brings it

nearer to a condition of equilibrium. As the attainment of equilibrium necessitates the precipitation of CuAl_2 from solid solution it may be inferred that the change in properties is connected in some way with the precipitation of this substance. The nature of this change will be discussed presently, but in the meantime the effect on the mechanical properties of the changes that take place with time at atmospheric temperature may be illustrated. These changes have a maximum effect on alloys containing about 4-4.5 per cent. of copper because this is the greatest amount that can be taken into solution during the solution treatment. They are greatly affected by the presence of certain other elements in addition to aluminium and copper, and alloys of high purity may first be considered. In such an alloy containing 4 per cent. of copper and 0.02 per cent. of iron plus silicon, heated at 500°C . for 20 hours and quenched, Gayler and Preston (115) found the Brinell hardness number to increase from 64 to 80 in three days at atmospheric temperature. Thereafter it continued to increase more slowly. Jeffries and Archer (116) who used an alloy of high purity containing 4.5 per cent. of copper obtained the following results after the treatments shown.

TABLE 28

<i>Condition</i>	<i>Tensile strength tons sq. in.</i>	<i>Elongation per cent. on 2 in.</i>	<i>Brinell hardness number</i>
As cast. Aged 2 days	9	7.5	45.6
Heated 1 hr. at 540°C ., quenched in water, aged 2 days.	14.6	5.5	76
Heated 8 hrs. at 540°C ., quenched in water, aged 2 days.	18	14.6	74.4
Heated 40 hrs. at 540°C ., quenched in water, tested immediately	16.2	20.7	62.4
Heated 40 hrs. at 540°C ., quenched in water, aged 2 days.	19	19.0	82.6

In the cast condition very little change would take place during the 2 days ageing, but after heating at 540°C . for 1 hour and quenching a certain amount of age-hardening occurred during the ageing period and as a result the tensile strength and Brinell hardness were increased. Keeping the other conditions constant and increasing the time of heating at 540°C . to 8 and then to 40 hours led to further increases in the hardness and strength attained after 2 days' ageing. This was due, of course, to the greater amount of CuAl_2 taken into solution before quenching, and the marked increase in elongation resulting from those treatments would be due to the virtual disappearance of the films of CuAl_2 which surrounded the crystals of the cast alloy. Comparison of the last two treatments illustrates the effect of the change with time at atmospheric temperature.

Phenomena similar to those described above are exhibited by numerous other alloys to a more or less pronounced extent. In

particular they are known to occur when certain elements are added to aluminium, copper, nickel, iron, lead, and zinc. Once a certain number of elements have been shown to produce the required effects when added to a given basis metal there is considerable scope for developing complex alloys by adding these elements in different amounts and combinations. Furthermore, other elements may be added to make it easier to retain the solid solution by rapid cooling or to accelerate or retard the change that is responsible for age-hardening. Finally, further additions may be made for purposes not directly connected with the ageing phenomena, e.g. to deoxidize, facilitate casting or machining, refine the grain size, &c. Commercial age-hardening alloys are consequently not simple binary alloys but, like commercial steels, usually contain a number of elements intentionally added besides the impurities usually present. In the case of aluminium, e.g., age-hardening effects are obtained when copper, magnesium, magnesium-silicide, or silicon is present, either alone or in various combinations, and manganese, iron, nickel, titanium, &c., are added for other reasons given in Chapter XVI. Owing to the fact that high purity aluminium was not available for making alloys when age-hardening first aroused attention in 1911, much of the work that has been done in the study of this phenomenon was performed on alloys containing a number of elements. Since this metal became available in 1926 a number of investigations have been carried out with a view to determining the individual effects of different elements and their mutual influence on each other. Nevertheless, much of the recent work has been performed on complex alloys of the types that have become established in industry. In the following discussion accordingly, points are illustrated by reference to alloys that are by no means simple binary alloys and in some cases not even aluminium alloys.

Like most other transformations in metals and alloys the age-hardening change is promoted by raising the temperature and retarded by lowering it. In alloys like those of aluminium and copper in which it proceeds at an appreciable rate at atmospheric temperature, it may be inhibited by keeping the quenched alloy in solid CO_2 (i.e. at $-72^\circ \text{C}.$). At this temperature the solid solution retained by quenching is persistent, i.e. it is unstable but cannot change because diffusion is impossible. Heating the quenched alloy above atmospheric temperature accelerates the change, and if this is high enough or the time long enough the hardness is found to rise to a maximum and then decrease. Thus with the alloy previously mentioned Gayler and Preston found the Brinell hardness (measured at atmospheric temperature) to increase from 64 to 108 in 8 hours at $200^\circ \text{C}.$ and then to decrease at a rate that reduced it to 88 in 120 hours. Heating a quenched alloy to accelerate the hardening change is known as artificial ageing or temper-hardening. The latter term is derived from the fact that tempering is the word used to describe the heating of quenched steel, and although objections

may be raised against its use in connexion with the heating of other alloys after quenching it is now widely employed. When the time and temperature of heating are such that the maximum on the time-hardness curve is passed the alloy is said to be 'over-aged'.

The relations between time, temperature, and strength or hardness have an important bearing on the mechanism of the constitutional changes that take place in retained solid solutions, and these relations as revealed in a number of extensive investigations carried out by various workers have been systematically

considered by Jenkins and Bucknall (117). The typical time-hardness curve for a quenched alloy of the type under consideration shows first an increase in hardness rising to a flat maximum and then decreasing as shown in Fig. 182. As the temperature at which the alloy is maintained after quenching is raised, the time taken to reach the maximum hardness decreases rapidly, and in many

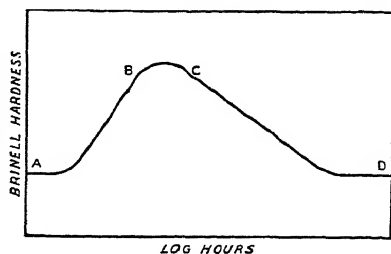


FIG. 182. Schematic diagram of hardness changes during age-hardening. (*Journal of the Institute of Metals.*)

investigations of age-hardening, part of the rising portion *AB* has been determined at low temperatures, part of the falling portion *CD* at high temperatures, and the curve as a whole has been determined at intermediate temperatures. Actually, however, the time-hardness curve has the same form at all temperatures, and this is revealed if experiments at low temperatures are prolonged sufficiently to pass the maximum and if those at high temperatures are shortened sufficiently to determine the ascending portion. A satisfactory set of curves obtained by measuring the change of tensile strength with time at different temperatures is shown in Fig. 183. These were determined by Bohner and refer to specimens of the aluminium alloy Lautal (4.5 per cent. copper, 2 per cent. silicon, and 0.5 per cent. manganese) subjected to a solution heat treatment and quenched. They show that, as the temperature at which the alloy is heated after quenching is raised from 85° C. to 220° C., the time taken to reach the maximum on the strength-time curve decreases. At the same time the magnitude of the strength at the maximum decreases.

Jenkins and Bucknall assembled the results obtained by a number of workers in systematic investigations of various alloys, viz. β -brass, copper-beryllium, copper-nickel-silicon, and several aluminium alloys. In many cases the experiments at low temperatures had not been sufficiently prolonged to attain the maximum on the time-hardness curves, while in those at high temperatures the specimens had not been examined after heating for periods short enough to give points on the ascending portion of the curves. The number of curves in which the maximum was shown was sufficient, however, to reveal the relations

between temperature and the time taken to attain the maximum. It was thus found that a straight line was obtained when the log of the time taken to reach the maximum strength or hardness was plotted against the reciprocal of the absolute temperature. The result of such a plot of the results given in Fig. 183 is shown in Fig. 184. Similar

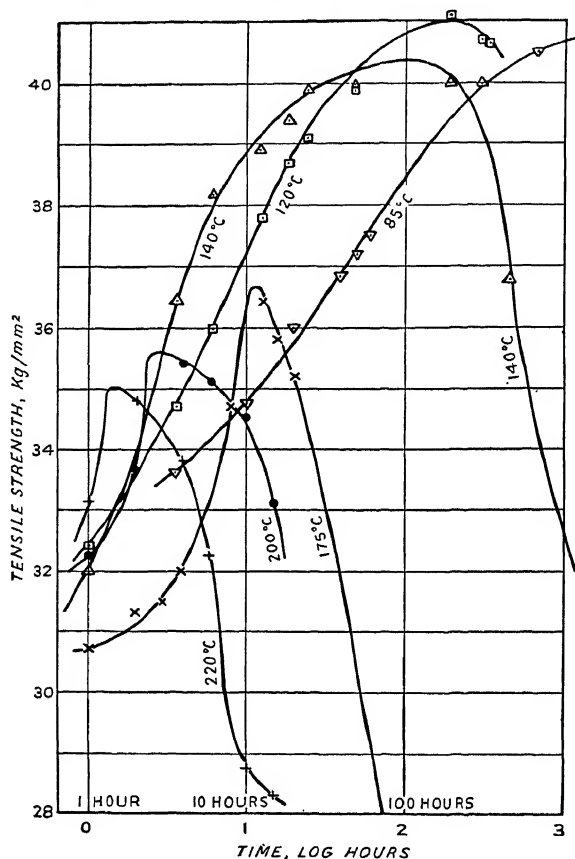


FIG. 183. Changes in tensile strength during ageing of the aluminium alloy 'Lautal'. (*Journal of the Institute of Metals.*)

results were obtained when this method of plotting was applied to other experimental data relating to the alloys mentioned above, and there is no doubt that the relations between the time taken to reach the maximum strength or hardness and the temperature of heating indicated by Fig. 184 are of general application. From this Jenkins and Bucknall deduce that the time taken to reach maximum hardness is connected with the temperature by the following equation:

$$t = Ce^{m/T},$$

where t is the time in hours, T the temperature in deg. absolute, and

m and C are constants. This relationship is valuable from a theoretical standpoint because it shows that age-hardening phenomena are subject to general laws which are fundamentally the same for all alloys and all temperatures. It is also valuable from a practical standpoint. In many investigations of these phenomena it has been the practice to measure the change in hardness taking place at convenient time intervals at arbitrarily chosen temperatures, and thus to assemble a mass of data that did not reveal what would occur with different times and temperatures and could not be used for the accurate comparison of one alloy with another. With a knowledge of the relations described above it is possible by determining two or three points on the line shown in Fig. 184 to deduce what will occur at other temperatures.

In Fig. 183 it is shown that the magnitude of the hardness at the maximum on the time-hardness curves decreases as the heating temperature increases. In the copper-nickel-silicon alloys studied by them Jenkins and Bucknall found that the maximum attainable hardness decreased linearly with increase in the heating temperature, and this

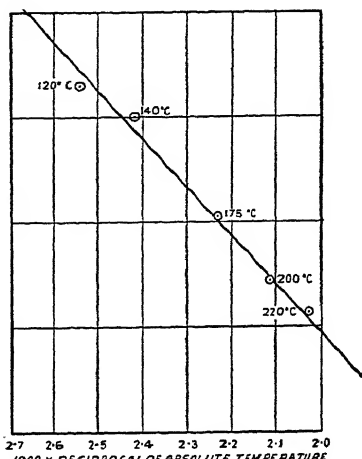


FIG. 184. Attainment of maximum tensile strength during ageing of the aluminium alloy 'Lautal'. (*Journal of the Institute of Metals.*)

result is confirmed by results obtained by Hansen on β -brass. Although this linear relationship between temperature and maximum attainable hardness is not so firmly supported as the relations between time and temperature, the evidence in favour of it is strong, and even if the linear relations are not generally valid there is no doubt that the maximum attainable hardness does decrease with the heating temperature. This is different from what was previously supposed, for, due to the long time necessary to reach maximum hardness at low temperatures, experiments have not been continued long enough to attain it, and thus a point on the ascending portion of the time-hardness curve at a low temperature has been compared with the maximum at a higher temperature to support the conclusion that the maximum attainable hardness first increases with the heating temperature and then decreases. This gave rise to the idea of a critical or optimum age-hardening temperature. From a scientific point of view this conception is not valid, but from a practical point of view it is of considerable importance because, although greater hardness may be obtained by ageing at lower temperatures the time taken to attain it may be impossibly long.

Alloys of the duralumin type (4 per cent. copper, 0.5 per cent.

magnesium, 0.3 per cent. silicon, and 0.5 per cent. manganese) are the best known of the age-hardening aluminium alloys. After quenching, they harden with time at atmospheric temperature, and it is generally supposed that the maximum hardness is reached in 3 to 5 days. Actually, however, hardening continues indefinitely, but after about 5 days the rate of increase is hardly perceptible. If experiments are conducted at higher temperatures, and the line shown in Fig. 184 determined and extrapolated to atmospheric temperature, it appears that about one million years would be required for the maximum hardness to be reached. This would be greater than that obtained at any higher temperature but the fact is of little practical importance, and consequently when the greatest hardness is required the alloys are heated to 150–200° C. at which the maximum is reached in a few hours.

One more aspect of the relations between hardness, time, and temperature may be mentioned. Gayler and Preston found that when the various alloys they used were quenched and aged at atmospheric temperature and then heated to 200° C. the first effect of the heating was to produce a decrease in hardness. Thus in an alloy containing 4 per cent. of copper and 0.46 per cent. of magnesium the hardness as quenched was 70, it rose to 108 during six days' ageing at atmospheric temperature, fell to 78 when the alloy was heated for 20 minutes at 200° C., then gradually rose to 115 during 5 hours' heating at 200° C., and finally began to fall slowly. The maximum hardness attained at 200° C. after 6 days' ageing at atmospheric temperature was the same as that attained when the alloy was heated at 200° C. immediately after quenching. The time to reach the maximum was also the same, viz. 5 hours in both cases. With other alloys, however, previous ageing at room temperature slightly decreased the maximum hardness attained at 200° C. and increased the time taken to reach it. In other investigations of less pure, and consequently more complex alloys, previous ageing at room temperature has been found to increase substantially the time taken to reach the maximum, and in many cases to decrease the hardness attained at the maximum.

As already stated the phenomena described above are now known to occur in a large number of alloys many of which are described in Parts V and VI. In the aluminium base alloys the necessary changes can take place at atmospheric temperature, but in many other alloys the solid solutions retained by quenching are persistent at atmospheric temperature and must be heated to enable the changes to proceed. This applies to the copper-beryllium, the copper-nickel-silicon, the copper-aluminium-silicon, and the iron-copper alloys. Furthermore, in aluminium and numerous other alloys quenching, or at least fairly rapid cooling, is required to retain the alloy in such a condition that substantial amounts of age-hardening can occur, but in iron-carbon-copper alloys even quite slow cooling suffices for this purpose. In all cases the age-hardening process is accelerated by deformation of the alloy after

quenching or otherwise cooling so as to retain the solid solution stable at high temperature. Sometimes the effect of deformation is small, while in other cases it is the controlling factor. This latter condition appears to be realized to a pronounced extent in steel, and thus the hardening effects seem to be more closely connected with deformation than with heat treatment, and in consequence the phenomenon is termed strain-ageing. In most cases of age-hardening the change suppressed by rapid cooling is one of solubility, but in some cases a change from one constituent to another or a eutectoid change is involved. Age-hardening of copper-zinc alloys takes place when the β - to α -change is suppressed, while in zinc-aluminium, copper-aluminium, and copper-tin alloys it occurs after a eutectoid change is suppressed. In zinc-aluminium alloys the change in the retained solid solution takes place at atmospheric temperature, in the other alloys the temperature must be raised. As shown in Fig. 179 copper-gold alloys near the CuAu composition are harder when the lattice structure is ordered than when it is disordered. As rapid cooling retains these alloys in the disordered condition, while subsequent heating at a suitable temperature permits them to attain the ordered condition, it follows that they will harden on heating after rapid cooling. These alloys and some others which undergo the same kind of change therefore behave in a similar manner to the alloys just described, but the phenomena on which the hardness changes depend are rather different in the two cases. In the following discussion of the mechanism of age-hardening disorder-order changes are not taken into account.

THE MECHANISM OF PRECIPITATION-HARDENING

The term 'ageing' should be reserved for treatments which consist of retaining metals at atmospheric temperature, and age-hardening should be used only to denote increase in hardness with time at this temperature. It might be used with equal justification to denote an increase in hardness following heat treatment or deformation, but for the sake of clarity it is desirable to use the term strain-hardening in the latter case. Heating a quenched alloy in order to accelerate or promote a hardening change may be called tempering, and the increase in hardness thus produced temper-hardening, but some term is required to denote the changes under consideration irrespective of whether they occur at atmospheric or higher temperature. The most suitable term for this purpose is 'precipitation-hardening'. This was first introduced when the increase in hardness was generally supposed to be due in all cases to an actual precipitation of the constituent retained in solution by rapid cooling. It has recently been objected to since it has been shown that at room temperature precipitation does not occur while the hardness is rising. This objection is not serious, however, for even if the increase in hardness does not actually depend on precipitation, it does depend on a change connected with precipitation.

In the hundreds of investigations that have been performed on precipitation-hardening it has been too often assumed that conclusions with regard to the mechanism of this phenomenon could be based on the results of strength or hardness measurements. Actually such determinations provide no reliable foundation on which to base deductions relating to constitutional changes. If a given treatment leads to an increase or a decrease in strength or hardness we know that some change in the constitution, microstructure, or crystal structure of an alloy has occurred, but we do not know what it is. If we know as a result of other studies that an increase in strength or hardness is usually associated with certain kinds of constitutional or structural changes, while a decrease is usually accompanied by others, we may in the absence of other evidence make a guess about the probable cause of the increase or decrease produced by the treatment under consideration. But it is better to try to obtain other evidence of a more decisive kind. Actually, microscopic examination, X-ray analysis, and specific volume and electrical resistivity measurements give more direct information about constitutional and structural changes than do determination of mechanical properties. In the more recent studies of precipitation-hardening all these methods and several others have been employed, and have given great assistance in attempting to explain the phenomenon, but so many alloys have been studied under so many different conditions, with (in many cases) such divergent results, that no entirely satisfactory explanation has yet been obtained of a process which to a large extent is not susceptible to complete investigation with available methods.

It is impossible to review all the experimental data relating to the mechanism of precipitation-hardening or to mention all the theoretical views that have been put forward, but on account of the importance of the subject it is necessary to present some kind of picture of what appears to occur. The phenomenon first aroused attention when Wilm found in 1911 that suitably treated aluminium alloys of the type now called duralumin increased in hardness with time at atmospheric temperature. The first explanation was put forward by Merica, Waltenberg, and Scott (118) in 1919. This took account of the following facts: (1) a supersaturated solid solution is retained by quenching, (2) this solid solution then changes in such a way that an increase in hardness occurs without a change in microstructure, and (3) under suitable conditions of time and temperature the increase in hardness is followed by a decrease, and when this has proceeded far enough particles of CuAl_2 can be seen under the microscope. As a change in the supersaturated solid solution would be expected to proceed in the direction of equilibrium and would thus involve precipitation of CuAl_2 , as particles of CuAl_2 could be detected when the change had proceeded far enough, and as it was known that larger particles are readily formed from smaller ones by a process of 'coalescence', it was reasonable to

conclude that the increase in hardness was due to precipitation of CuAl_2 in the form of small particles and the subsequent decrease to their growth. This may be described as the simple precipitation theory. For many years it was not seriously challenged, and even now such modified ideas as have been suggested by later work are for the most part elaborations of this simple explanation rather than alternative theories.

In general, the presence of a given amount of an element in solid solution in the basis metal should decrease the electrical conductivity to a greater extent than the presence of the same amount in the form of isolated particles of an intermediate constituent. Thus the precipitation of CuAl_2 from a supersaturated solution of copper in aluminium should be accompanied by an increase in electrical conductivity. Several workers have shown, however, that during the room temperature ageing of aluminium-copper alloys (or duralumin) the conductivity actually decreases. At higher temperatures the conductivity increases during hardening, but sometimes the increase is preceded by a decrease. Precipitation of CuAl_2 from solution should also be accompanied by an increase in specific volume, but several workers have shown that during the room temperature ageing of copper-aluminium alloys or duralumin no increase in specific volume occurs. Furthermore, on heating, the specific volume does not begin to increase until the maximum hardness is passed.

When two phases are present in an alloy the characteristic lines of each should appear in an X-ray spectrogram. But as the strength of the lines characteristic of a phase depends on its amount and the size of the particles, a small amount of a finely dispersed phase will not be definitely shown on an X-ray spectrogram. The solution of copper in aluminium results, however, in a contraction of the aluminium lattice, and the precipitation of this as CuAl_2 should permit the lattice constant to return to the value characteristic of aluminium. Thus although failure of the X-rays to detect positively the presence of CuAl_2 does not prove that none has been precipitated, absence of expansion in the lattice should indicate that no precipitation has occurred and *vice versa*. In general, X-rays do not show the presence of CuAl_2 until this is already visible under the microscope, but they can follow minute changes in the lattice of the solid solution, and the results show that during room temperature ageing no change in lattice parameter occurs, and even at higher temperatures the lattice does not expand to the dimensions characteristic of aluminium until the maximum hardness has been passed. Hengstenberg and Wassermann (119) have shown, however, that during the room temperature ageing of duralumin the character of the lines on the X-ray spectrograms changes in a way that indicates an alteration in the distribution of the copper atoms in the solid solution.

In the light of the data that have been accumulated since 1926 it is now generally held that the age-hardening of aluminium-copper alloys

or duralumin at room temperature does not involve precipitation of CuAl_2 in any form and is thus due to some change in the solid solution that precedes precipitation. At higher temperatures precipitation occurs, but the greatest hardnesses are reached before it occurs. Other alloys have not been so carefully studied as these, but in some, e.g. copper-nickel-aluminium, copper-nickel-silicon, and iron-nitrogen alloys, the cause of hardening is evidently the same as in duralumin at atmospheric temperature, while in others, e.g. copper-beryllium, silver-copper, aluminium-silicon, aluminium-magnesium, iron-molybdenum, and iron-tungsten, actual precipitation occurs while the hardness is increasing. There are at least two different ways of regarding the available evidence. It may be held to show that the ageing of duralumin at atmospheric temperature depends on one kind of phenomenon and that of copper-beryllium alloys at 200°C . and above on another. Alternatively, a general explanation applicable to all cases may be sought. It is practically certain that the fundamental changes involved in the decomposition of solid solutions retained by quenching are the same in all cases. It is equally certain that these changes are affected by the nature of the alloy, time, and temperature. In this sense, then, there is a general explanation applicable to all cases, but the exact conditions on which the hardness of a given alloy after a given treatment depends may vary from case to case.

In the section on 'Diffusion' a concentration gradient was supposed to exist in all cases, i.e. when atoms are diffusing from the environment into a metal, when a heterogeneous solid solution is proceeding towards equilibrium, when a constituent is going into solution, and when crystals of a constituent are growing. When an aluminium alloy containing 4 per cent. of copper is cooled to 500°C . it becomes supersaturated with copper and under equilibrium conditions CuAl_2 begins to form. Before any crystals of CuAl_2 appear the alloy is a homogeneous solid solution in which there is no concentration gradient. Yet once the alloy is cooled below 500°C . it is unstable and the interchanges of positions among the atoms will tend to take place in such a way that the strain caused by the excess solute atoms is released by their rejection from the crystal lattice. This leads to diffusion even when no concentration gradient exists. As, however, the excess solute cannot be rejected from the metal the only way in which adjustments can take place is by the diffusion of the solute atoms to points where they produce less strain. Such points are provided by the crystal boundaries, and a characteristic feature of changes in solid solubility is the accumulation of solute atoms there. This leads to the appearance of the new phase at the boundaries of the existing crystals, but nothing is known about the exact steps that intervene between the arrival of excess solute atoms at the crystal boundaries and the appearance of the new phase there. Can one copper atom form a minute crystal of CuAl_2 with two adjacent aluminium atoms, or must the requisite concentration of copper and aluminium

atoms be built up over a certain area before this changes as a whole to CuAl_2 , and if so how many molecules of CuAl_2 are required to form a crystal nucleus? All we know is that the instability of the solid solution crystals leads to rejection of solute atoms to the crystal boundaries where crystals of the precipitating phase begin to form. As shown, however, by the frequent occurrence of the Widmanstätten structure, the crystal boundaries are not the only points at which the solute atoms may tend to accumulate in order to reduce the strain in the lattice as a whole. Evidently they may also tend to accumulate along certain crystallographic planes where crystals of the precipitating phase begin to form.

Under equilibrium conditions of cooling the beginning of the change in the supersaturated solid solution involves (1) the rejection of an infinitely small amount of the solute atoms to the crystal boundaries and certain crystallographic planes, and (2) the immediate formation of crystals of the precipitating phase. Thereafter as the temperature falls, solute atoms diffuse towards the existing crystals of the precipitating phase and cause them to grow. When, however, the 4 per cent. solid solution of copper in aluminium is retained at atmospheric temperature by quenching, the conditions are quite different from those existing in this same solid solution when it begins to deposit CuAl_2 during cooling under equilibrium conditions. In this case the solution is highly supersaturated and nearly all the solute atoms are in excess. Furthermore, the mobility is low and appreciable diffusion over long distances cannot occur. Under these conditions it is reasonable to expect that changes which differ from those that take place during cooling at the equilibrium rate will occur. We have seen that in crystals containing two sorts of atoms ordered structures are more stable than disordered. Furthermore, we have seen that when the conditions do not permit a precipitating constituent to diffuse to the crystal boundaries, it tends to precipitate on certain crystallographic planes. The relative proportions of copper and aluminium atoms in the alloy under consideration do not permit the formation of an ordered structure of the type previously described, but the interchanges of positions among the atoms may lead to the concentration of copper atoms on certain crystallographic planes. Thus the changes that occur at atmospheric temperature in the alloy under consideration are probably due to a type of disorder \rightarrow order change, which is also a preliminary step towards the precipitation of CuAl_2 on the crystallographic planes. It is difficult to discover what takes place when the orderly distribution of copper atoms changes to an actual precipitate, but the important point is that precipitation is preceded by another change.

In the solid solution of copper in aluminium the change in the distribution of the copper atoms can take place at atmospheric temperature but the precipitation of CuAl_2 cannot occur to any substantial extent. Such changes in hardness, strength, and other properties as are observed

in this alloy must therefore be due to the change in the distribution of the copper atoms. The fact that the hardness and strength may rise without precipitation taking place proves that this rise is caused by a change that precedes precipitation. Even if it is shown that some precipitation occurs while the hardness is rising, this does not prove that the increase in hardness is caused by precipitation rather than the change which precedes it. For once it has been shown that a change which precedes precipitation can cause a rise in hardness, it is necessary to show that the hardness remains high after most of the solute is precipitated before it can be proved that precipitation may also produce a rise in hardness.

In the aluminium-copper solid solution the change that precedes precipitation can proceed at atmospheric temperature without any precipitation taking place. If, however, the solid solution after quenching is heated to a suitable temperature, CuAl_2 is precipitated in the form of minute particles which subsequently increase in size by 'coalescence'. Under these conditions, however, precipitation is no doubt preceded by the same change as at atmospheric temperature. Thus, considering the whole change from the initial state obtained by quenching to the final state obtained by tempering we may say that three processes are involved: (1) a change preceding precipitation, (2) actual precipitation, and (3) growth of the precipitated particles. The relations between these three processes are controlled by temperature, the nature of the basis metal, and that of the other elements present, and these relations in turn control the alterations in properties that accompany the changes.

During room temperature ageing of aluminium-copper alloys the change that precedes precipitation takes place alone. This begins slowly, proceeds gradually, continues more rapidly, and finally falls off with time. Two factors may enter into the gradual nature of this change: (1) at any given point it may proceed at a certain rate, and (2) it may extend at a certain rate from point to point throughout the alloy. Both factors no doubt enter into the process, but it seems that the second is the more important. Thus, in general, the properties will be mainly influenced by the extent to which the change has taken place throughout the alloy, and in a lesser degree by the stage reached at the numerous points concerned.

If the alloy is heated to, say, 100°C . immediately after quenching and is maintained there, the change that precedes precipitation is accelerated, i.e. it extends more rapidly from point to point and proceeds more rapidly at each point. The process of actual precipitation is also accelerated and now takes place at a measurable rate. If we consider any one point in the alloy we can say that the sequence of changes is, firstly, an alteration in the distribution of the copper atoms preceding precipitation, and secondly, precipitation of a minute particle of CuAl_2 . The resistance to deformation at this point is probably a maximum when the change that precedes precipitation is just com-

pleted. It decreases when precipitation actually takes place. If we consider the alloy as a whole we can say that at any instant after the changes have commenced there are in general three different kinds of points: (1) those where conditions are substantially the same as when the alloy was quenched, (2) those where the change that precedes precipitation has occurred, and (3) those where precipitation has occurred. The hardness and other properties will depend on the relative numbers of the different kinds of points in the alloy and these in turn depend on the relative rates of the two changes, i.e. (a) preceding precipitation, and (b) precipitation.

We have stated above that actual precipitation results in a decrease in hardness compared with that produced by the preliminary change. It is difficult to say, however, just what this means. The transition from an accumulation of copper atoms along certain planes to layers of CuAl_2 along those planes may not involve a decrease in hardness, and may actually involve an increase. Once the CuAl_2 lattice has been established at certain points, however, copper atoms from regions where the preliminary change has taken place will diffuse towards the CuAl_2 , and this will lead to a decrease in hardness. Thus newly precipitated particles may not lead directly to a decrease, but they produce conditions which soon result in this.

The three changes involved in the transition from the quenched to the finally tempered condition are differently affected by temperature and the nature of the alloy. In aluminium-copper alloys at atmospheric temperature the first change takes place alone and a very high hardness would ultimately be reached if the experiments could be continued long enough. At temperatures above atmospheric this change takes place more rapidly, but it is followed by precipitation which tends to counteract its effect on hardness. This in turn is followed by coalescence which tends further to decrease the hardness. At any given instant the hardness depends on the stage reached by the various changes throughout the alloy as a whole. The maximum hardness at any given temperature is reached when the number of points at which the preliminary change has reached completion is a maximum. Thereafter the hardness falls as a result of precipitation at these points and coalescence of the precipitated particles. The maximum hardness reached at elevated temperatures is lower than that which would ultimately be reached at atmospheric temperature, because precipitation reduces the number of points at which the preliminary change can simultaneously reach completion, and because it produces conditions which facilitate movement of copper atoms from positions in the aluminium lattice to the growing crystals of CuAl_2 . At atmospheric temperature the number of points at which the preliminary change has taken place increases progressively. At higher temperatures the increase in the number of such points is offset by precipitation.

The change in properties exhibited by a given alloy at a given

temperature depends on the relative rates of the three constitutional and structural changes. The lower the temperature the greater the extent to which points where the preliminary change has taken place may accumulate. The higher the temperature the more closely does precipitation follow the preliminary change and the more closely does coalescence follow precipitation. Thus the maximum hardness attainable decreases as the temperature is raised. Owing to the time taken to reach the maximum attainable hardness it is never reached at temperatures low enough to prevent actual precipitation, so that the maxima actually reached depend on the accumulation of points where the preliminary change has taken place and that of newly precipitated particles. In the first stage of the change these accumulations rise to a maximum and so does the hardness. In the later stage they decrease as a result of growth and coalescence of CuAl_2 . In aluminium-copper alloys at room temperature the preliminary change can take place at an appreciable rate without the others. At higher temperatures it is accompanied by precipitation and at still higher temperatures by coalescence. In certain other alloys the preliminary change may take place at an appreciable rate without the others at a suitable elevated temperature while at still higher temperatures all three changes may take place. In other alloys, however, there may be no temperature at which this change takes place alone at an appreciable rate. Thus, in general, the rise in hardness up to the maximum may be due to (1) the preliminary change, or (2) the preliminary change accompanied by precipitation that is slow enough to allow the product of the preliminary change to accumulate. The maximum hardness is attained when the change in distribution of the copper atoms has occurred at the maximum number of points, and in so far as precipitation consists of a transition from concentrations of copper atoms on certain planes to layers of CuAl_2 , on these planes it has substantially the same effect as the preliminary change. Once the CuAl_2 lattice has been established, however, copper atoms can diffuse from regions where the preliminary change has taken place towards the CuAl_2 crystals, and this results in a decrease in hardness. At any temperature at which the preliminary and subsequent changes can both take place the hardness reached depends on the relations between them.

In conclusion it is worth while to apply the above explanation to the results obtained when an alloy is aged at room temperature and then heated to a higher temperature. In aluminium-copper alloys the change that precedes precipitation proceeds at atmospheric temperature and this is accompanied by an increase in hardness. When the alloy is heated to a higher temperature the conditions are favourable for precipitation and growth of the precipitated particles at points where the preliminary change has already taken place. This tends to result in a decrease in hardness. If the temperature is high enough to allow the subsequent changes to proceed rapidly at points where the

preliminary change has reached the necessary stage, the hardness will fall below that reached during room temperature ageing. Thereafter, however, the hardness will increase as a result of the continuation of the preliminary change at points where it has not yet reached the stage necessary for precipitation. The conditions are then the same as would be realized had the alloy been heated to 200° C. immediately after quenching except for the fact that the precipitation change is advanced by the precipitation of CuAl_2 at the points where the necessary conditions were realized during previous ageing at room temperature. At these points the only change that can take place at 200° C. is coalescence which leads to a reduction in hardness, and as all these points are, as it were, eliminated from the system as far as an increase in hardness at 200° C. is concerned, the total number of points at which conditions producing maximum hardness can be realized is decreased. Thus the increase in hardness that occurs at 200° C. after the initial softening on first heating does not in general reach the same maximum as is reached on heating at 200° C. immediately after quenching. Whether the alloy was previously aged at room temperature or not, the progress of the changes in one direction eventually leads to a condition in which the number of points at which the preliminary change is proceeding or has reached completion begins to decrease, and shortly afterwards the number of newly precipitated particles also begins to decrease. The hardness then begins to diminish and continues to do so until the structure consists of moderately large globules of CuAl_2 in a matrix of aluminium containing 0.5 per cent. of copper in solid solution.

PART III

PROPERTIES OF METALS

CHAPTER VII

GENERAL CONSIDERATION OF PROPERTIES AND MECHANICAL TESTING

GENERAL CONSIDERATION OF PROPERTIES

IN this book we are mainly concerned with those properties of metals that influence their behaviour in service or during the operations performed in preparing them for service, and are not directly concerned with those that come into play in extracting and refining them. Most metals are molten at the end of the manufacturing operations and alloys are prepared by mixing metals in the molten condition. A metal or alloy may be said to be made when a melt of the requisite composition has been prepared. It is then poured into a mould and allowed to solidify and it is at this point that it comes within the scope of this book. As, however, its behaviour during casting, in all subsequent operations, and in service, may be affected to a pronounced extent by the conditions which obtain in the molten metal just before it is cast, some consideration of the molten stage is necessary. This aspect of the subject is dealt with in Part IV. In the meantime attention may be confined to those properties that come into play after the metal leaves the melting furnace.

In considering the properties of metals it is necessary to take account of the different meanings the term may have. In the first place, it may be used to denote the specific attributes of metals that are alternatively called physical constants, e.g. density, melting-point, boiling-point, specific heat, latent heat of fusion, linear coefficient of expansion, electrical resistivity, magnetic susceptibility, &c. These properties are capable of more or less exact measurement and expression in terms of some unit such as grammes per c.c., degrees centigrade, calories per gramme, cm. per cm. per °C., ohms per cm.³, &c. The term may also be applied, however, to what are in effect simply aspects of the behaviour of metals when subjected to certain conditions. The yield-point, ultimate tensile strength, elongation, hardness, resistance to impact, endurance limit, and limiting creep stress, are properties of this kind. All these quantities depend on some fundamental attributes of the metal, but at present they cannot be measured, so the metal is subjected to a certain treatment; certain measurements that indicate its behaviour during this treatment are made, and the quantities thus measured are given a name and called properties. Finally, the term is applied to whole

groups of attributes that combine to influence the behaviour of the metal under certain conditions. Thus all the properties such as melting-point, latent heat of fusion, fluidity when molten, shrinkage at solidification, solubility for gases, and strength at temperatures just below the melting-point, are included in the term 'casting properties', while all the measurements made when metals are subjected to stress are included in the term 'mechanical properties'. It is this last use of the term that is most convenient for the present purpose.

As shown in the schedule given in Chapter I, the properties finally obtained in a metal or alloy depend in the first place on its composition and in the second place on its treatment. The composition is fixed when the metal leaves the furnace and this, within certain limits, determines the properties obtainable. Inside these limits the properties finally obtained can be varied by means of treatment. The relations between composition and properties are considered in Parts V and VI. The influence of treatment within the limits in which it is effective may be mentioned here. The operations that are included in treatment are carried out with two main objects: (1) to bring the metal to the required shape, and (2) to produce in it the properties required in service. The major operations are casting, hot-working, and cold-working, and these with the heating operations that accompany them affect both shape and properties. Heat treatments of the type described in Chapter VI have a pronounced influence on properties, but have nothing to do with shaping, while machining is an important method of shaping but has nothing to do with properties. In addition to these major treatments metals are subjected to a variety of operations designed to produce articles of the required size and shape or to induce in them the desired properties. The production of the shape is sometimes achieved by the joining together of parts of simple shape by welding, soldering, or brazing, and the properties are sometimes obtained by means of surface treatments such as carburizing, nitriding, anodic oxidation, electro-deposition of nickel or chromium or coating with zinc or tin by dipping. The properties that influence the preparation of metals for use are those that come into play in the above operations and thus it is customary to refer to casting, hot-working, cold-working, machining, heat treating and welding properties, and to take account of the behaviour of metals in soldering, brazing, electroplating, dipping, and other surface treatments.

The industrial application of metals is influenced by their response to the treatments mentioned above and by the properties displayed by the finished articles. Certain applications of certain metals depend mainly on one specific attribute, while others depend on a combination of properties. In some cases the need for a certain attribute is so important that cost is hardly considered, but in general the cost of the finished article has a marked influence on its application. As examples of applications in which one specific attribute is of outstanding

importance mention may be made of the use of tungsten for the filaments in electric lamps where its high melting-point ($3,400^{\circ}\text{C.}$) is the controlling factor, the use of the iron-nickel alloy 'Invar' in instruments, standard bars, and measuring tapes where its zero coefficient of expansion is the controlling factor, the use of the iron-nickel alloy Permalloy for magnetic purposes where its high permeability is the controlling factor, and the use of copper where its high electrical conductivity is required. In general, most applications of metals depend to a large extent on one set of properties, but the predominance of any one group of attributes is generally less pronounced than in the above examples. Thus, if the special varieties known as Stainless and Magnet steels are excluded, steel in general may be said to be used because of its mechanical properties, but its cheapness compared with the non-ferrous metals is also important. Similarly, cast iron may be said to be used generally because of its casting properties, but it would not thus be used if it did not possess the necessary mechanical properties. In the same way pure aluminium is distinguished by its high electrical conductivity, certain alloys have conspicuously good casting properties and others good working properties, all are notable for their lightness and some for their high resistance to corrosion, but in almost every application their mechanical properties have also to be considered.

The specific properties exhibited by the different metals and alloys after different treatments are dealt with in Parts V and VI, and these treatments and the properties on which they depend are considered in Part IV. The purpose of this part is to consider such general aspects of the properties of metals as have not been discussed in Chapters III and IV, and do not come within the scope of Parts IV to VI. These relate to mechanical and chemical properties. The former control the response of metals to applied force, the latter their response to the chemical action of the environments to which they are exposed. Both groups of properties come into play in the treatment as well as in the use of metals. Hot-working, e.g., depends on the mechanical properties of metals at elevated temperatures, cold-working depends on their mechanical properties at room temperature, and the effect on the metals of the atmospheres to which they are exposed during heat treating and working operations depends on their chemical properties. Mechanical properties are dealt with in this chapter and chemical properties in Chapter VIII.

MECHANICAL PROPERTIES AND TESTING

In Chapter III it is stated that the mechanical properties are those that determine the response of metals to applied force and that four different aspects have to be taken into account: (1) the phenomena on which the response to applied force ultimately depends, and (2), (3), and (4) the relation of these to use, preparation for use, and testing respec-

tively. The phenomena on which the response to applied force ultimately depends are considered in Chapters III and IV. The other aspects remain to be dealt with. Of these, behaviour in use and in preparation for use are considered in terms of the performance observed in different applications or in different fabricating operations. This is discussed in Parts IV to VI. The fourth aspect, testing, is, however, closely connected with all the others and it is to it that most of this chapter is devoted.

In service and in fabricating operations complicated combinations of stresses are applied under varied conditions, and while in service the metals are required to withstand the stresses without deforming or fracturing, in fabrication they are required to deform readily without fracturing. In order to discover exactly how a metal will behave under given conditions of service or in a particular deforming operation it is necessary to try it, but some preliminary indication of its suitability can be obtained by means of tests. These are based in the first instance on an analysis of general service conditions. Thus it may be said, that in service metals are subjected to various combinations of tensile, compressive, flexural, torsional or shearing stresses which may be applied at different rates, for different lengths of time, at different intervals of time and at different temperatures. In any one application, however, rather simpler conditions are realized, and it is usually possible to say that a given component is subjected to a constant tensile or compressive stress applied for a long time at a given temperature, to the repeated application of a range of stress that varies from a certain value in compression to another value in tension, or to the repeated application of combined torsion and bending and so on. In tests, still simpler conditions are, or may be, realized, and the behaviour of the metals under these conditions may be used as a guide to their behaviour under the more complicated service conditions. There is, however, another aspect of testing. All features of the behaviour of metals under stress ultimately depend on the same intrinsic attributes, and consequently, although test conditions may differ considerably from service conditions, the results obtained under one set of conditions indicate what may be expected under the other.

When the methods of mechanical testing are considered as a whole in relation to the purposes for which they are used it is evident that both the above-mentioned aspects of testing are taken into account, but their relative importance varies considerably in different tests. In recent years a number of special methods of testing have been devised to determine the relative behaviour of different materials when used for spiral and laminated springs, wire-ropes, chains, boiler-plates, rails, tyres, gears, &c., or to determine the suitability of different metals for cold-pressing operations. In these tests attempts are made to imitate the service conditions either accurately or as far as is consistent with controlling the conditions and obtaining quantitative results. The

most commonly used tests do not, however, depend for their significance on the extent to which they imitate service conditions. They depend on the fact that the quantities measured in the tests are related to the fundamental mechanical properties of the metal and through these to the service conditions. This applies to the tensile and the hardness tests which are the standard methods of testing, and also perhaps to the impact test which is gradually increasing in importance. The only quantities determined in the tensile and hardness tests that have a direct bearing on service conditions are the elastic limit, yield-point, or proof stress. These indicate the stress at which substantial deformation begins and therefore the highest static stress that should be applied at atmospheric temperature. The percentage elongation, reduction in area, ultimate tensile stress, and hardness number have a bearing on the behaviour of metals in deforming operations, but they have no direct relation to service conditions in which stability and rigidity are required. Nevertheless, these quantities are recognized to be of great importance in preparing designs and specifications and in comparing materials.

Fatigue, corrosion-fatigue, and creep tests represent a type of test which is intermediate between the two just mentioned. They imitate service conditions more closely than the tensile test because they take more factors into account, namely, the effect of repeated stressing, the effect of the environment in which this is carried out and the effect of time where this is important. But in general no particular service conditions are closely imitated. When this is attempted, as in the testing of springs in special fatigue machines, the test falls into the same class as the above-mentioned tests of chains, wire-ropes, &c., but when fatigue or creep tests are applied to specially prepared specimens in standard types of machines the object is generally to obtain a result that can be used to compare the material tested with other materials previously tested, and to arrive at an estimate of the suitability of this material by reference to previous experience of the relations between behaviour in service and results obtained in the test.

We know from experience that some metals can be hot-rolled while others cannot, that some can be forged with ease and others with difficulty, that some can be cold-drawn and others pressed, and that for each service application some metals are suitable while others are not. All the quantitative data on the mechanical properties of metals are obtained, however, by means of tests, and the relations between these data and behaviour in service or in working operations are very complicated. In general it may be said that the connexion between test results and behaviour cannot be formally established by argument, and consequently the validity of test results rests on some combination of the following:

1. The conditions realized in the test resemble those realized in a particular treatment or application.

2. The behaviour in the test depends on the same ultimate attributes as the behaviour in treatment or service.
3. Experience having shown that a metal which gives certain results in the tests gives satisfactory performance in service, it may be inferred that all consignments of this metal that give these same results will behave similarly under the same conditions of service, and, with less probability, that a different metal that gives closely agreeing test results will also behave similarly.

The results obtained in mechanical tests are used for a variety of purposes. In the first place, they are used in connexion with specification and acceptance. When it has been established that a given metal after a given treatment gives satisfactory performance in a particular application, and its yield-point, tensile strength, elongation, reduction in area, and hardness are known, a specification which states that all metal intended for this application should have a given composition and give certain results in the specified tests is prepared, and the metal is only accepted for use if it satisfies this specification. Further uses of test results arise out of this. If another metal gives superior test results to those already known to be satisfactory for a given application, then this other metal may be even more satisfactory, and if no consideration of cost arises it may be given a trial. Owing, however, to the fact that tests are at best only indirectly related to service performance, this trial may not be satisfactory, and therefore the reluctance to try new metals increases as the consequences likely to result from unsatisfactory performance become more serious. Another use of tests is in connexion with the control of treatment. As treatments are performed to develop the properties necessary to meet particular specifications, mechanical tests are one of the most obvious methods of ascertaining whether the treatment is being satisfactorily carried out. As the results of such tests are the only quantitative data obtained about the mechanical properties of metals, they are widely used in comparing one metal with another and in investigating the effects of composition and treatment. Finally, as tests are methods of subjecting metals to stress under controlled conditions, they are the means employed in investigating the fundamental phenomena associated with response to stress. Thus, most of our information about the relations between stress, time, and temperature on the one hand, and deformation and fracture on the other, has been acquired by subjecting metals to different mechanical tests.

In this book we are mainly concerned with testing as a means of comparing one alloy with another, of illustrating the effects of different treatments, and of studying the relations between stress, deformation, and fracture. We are not directly concerned with acceptance testing. It must be pointed out, however, in connexion with this that the relations between the test-pieces and the articles intended for service are a matter of great importance. In the case of wire, rod, sheet, and strip, portions of the finished product may be cut off for testing. In

other cases, however, this is impossible. With castings, e.g., the test-pieces may be cast separately from the actual casting but from the same metal. They indicate the properties of the metal when cast as a test-bar and therefore serve to show how the metal compares with that previously used, but they do not indicate the properties of the casting as a whole which will be different in thin and thick sections and vary from the surface to the centre of heavy sections. Alternatively, the test-bars may be cast as part of the casting and then cut off. In this case the bars cast on different castings are not directly comparable and again they do not give the properties of different parts of the casting. Similar considerations apply to forgings, and there is considerable variation in the extent to which the test-bars resemble the forging. Further aspects of this question are discussed in Parts IV to VI.

THE TENSILE TEST

Of all the tests used in connexion with specification and acceptance, the investigation of the effects of composition and treatment, and the study of the phenomena of deformation and fracture, the tensile test is most widely employed. Not all tests in which tensile stress is applied are referred to as tensile tests. Thus, if a constant tensile load is applied for a long time and extension with time is measured, the test is called a creep test, and if a range of tensile stress is repeatedly applied the test is called a fatigue or endurance test. In the tensile test proper a gradually increasing tensile load is applied until the specimen breaks, and as the time taken to perform the test is a matter of minutes it is sometimes called the short-time tensile test to distinguish it from others in which a tensile stress is applied under different conditions.

The method employed in carrying out a tensile test and the behaviour of metals in this test are considered in detail in Chapter III. In a complete test the load is gradually increased while the resistance to deformation is increasing and then decreased when the resistance to deformation begins to decrease. At intervals throughout the test the length between two gauge marks is measured and at the conclusion of the test the stress, i.e. the load at any instant divided by the original cross-sectional area, is plotted against the extension expressed as a percentage of the original length between the gauge marks. In this way curves like those shown in Figs. 27 (copper) and 32 (iron) are obtained. It will be seen that the load (or stress) rises to a maximum at f in Fig. 27 and this is known as the ultimate tensile stress. The total percentage extension at the time of fracture is known as the elongation, and the difference between the original and the final cross-sectional area at the point of fracture expressed as a percentage of the original area is known as the percentage reduction in area. This last quantity cannot be deduced from a curve like that shown in Fig. 27, but is obtained after fracture by putting the two parts together and measuring the diameter

at the point of fracture. The percentage elongation also is usually obtained by measuring the length between the gauge marks after the fractured ends have been put together.

The three quantities mentioned above are easily determined and it is not necessary to trace out the curve to get them. The reduction in area and elongation may be calculated from measurements made before and after the test, and the ultimate tensile strength is obviously shown in the course of the test even when it is carried out very rapidly. In one respect the curve shown in Fig. 32 differs to a pronounced extent from that shown in Fig. 27. Up to the point *Y* very little extension occurs, but when the stress attains the value represented by *Y* the metal stretches rapidly and under a decreased stress until it reaches *K* when the relations between stress and extension become the same as those shown in Fig. 27. The stress at point *Y* is known as the yield-point stress and is clearly that at which appreciable extension begins. This stress also is comparatively easy to determine because the lever arm used in measuring the load (Fig. 25) drops on to the stop when the load that the specimen can sustain falls below that actually applied. Stress-strain curves of the type shown in Fig. 32 are, however, only given by polycrystalline specimens of iron and some of its alloys when in certain conditions and when tested below 350° C. The sudden yield is associated with aggregates of iron (or ferrite) crystals that have not been substantially cold-worked. Thus while it is shown by undeformed pure iron it is not if the iron has been cold-worked, and while it is shown by carbon steels in the cast, rolled, normalized or annealed condition it is not shown by them in the cold-worked or quenched condition. As tempering after quenching gradually transforms the martensite into ferrite and cementite, it also gradually restores the sudden yield-point, and in the same way heating cold-worked iron or steel promotes recrystallization and restores this point.

The yield-point is clearly of great importance in connexion with the use of metals for there are few applications in which substantial deformation can be permitted. Steel in such a condition that it gives a sudden yield-point constitutes the greater proportion of the metal used, but heat-treated and cold-worked carbon and alloy steels and numerous alloys based on copper, aluminium, nickel, and magnesium are used for constructional purposes. In connexion with the use of these metals it is convenient to measure some quantity that will have a similar significance to the yield-point in steel. This is done by specifying a certain permanent extension and calling the stress that produces it the yield-point or the proof-stress. Thus in testing non-ferrous metals which give curves of the type shown in Fig. 27 the stress that produces a permanent extension of 0.2 per cent. is called the yield-point or proof-stress, while in testing quenched and tempered steels the stress that produces a permanent extension of 0.1 per cent. is sometimes taken as the proof-stress.

Another measurement that may be made in tensile tests is the limit of proportionality, i.e. the stress at which the extension ceases to be a linear function of the stress. Elastic extension is a linear function of the stress while permanent extension is not, therefore if the first departure from the linear relationship is detected the limit of proportionality is the elastic limit. In practice, the point at which the curve is observed to depart from a straight line depends, however, on the sensitivity of the extensometer. The more sensitive this is the lower the stress at which the limit of proportionality is detected, and the nearer it approaches the true elastic limit when such exists. There is some doubt as to whether there is such a feature as a true range of elasticity, and it is probable that if the sensitivity of extensometers could be increased indefinitely permanent deformation would be shown to be begin at progressively lower stresses. Even moderately sensitive extensometers are able to show that soft metals like copper, gold, silver, and aluminium, have no range of elasticity in the primitive state, i.e. when not affected by previous deformation. When these metals have been strain-hardened, however, the most sensitive extensometers fail to detect permanent deformation below a certain stress. This applies also to iron and nickel alloys in the primitive state and to many alloys of copper and aluminium. In these cases it is impossible to show by extension measurements that there is no true range of elasticity. The fact that the range of elasticity becomes smaller and smaller as the sensitivity of the extensometer increases suggests this, however, and this indication is confirmed by measurements of damping capacity. Although it may therefore be concluded that metals in general have no true range of elasticity in the strictly scientific sense, the apparent limit of proportionality determined with an extensometer of given sensitivity is an indication of the value of the stress below which no substantial amount of permanent strain occurs. It is therefore a useful measurement from the point of view of design. Because of the indefinite nature of measurements of the limit of proportionality there is, however, a marked tendency to attach less importance to it and to use the proof-stress as an indication of the point at which appreciable permanent strain begins. As Chapter III is mainly devoted to a discussion of the tensile test and the behaviour of metals when stressed under these conditions, no further description of this test is required.

HARDNESS TESTS

There is no single method of testing which gives a result that can be said to express all that is implied by the term hardness which in practice is taken to mean resistance to penetration, to scratching, to abrasion, to cutting, to deformation, and so on. Throughout this book hardness has been taken to mean resistance to deformation. Thus when the resistance to deformation increases during a tensile test the

metal has been said to strain-harden, and the ultimate tensile stress which is a measure of resistance to deformation has been regarded as a measure of hardness. With equal justification, however, resistance to scratching, to abrasion, or to cutting might also be accepted as a measure of hardness and sometimes is so regarded, but in general what is called hardness is resistance to penetration. A ball, a cone, or a pyramid is forced into the metal under a given load and the size of the impression is taken as a measurement of hardness. In other words, the metal is deformed in a certain way under controlled conditions and the quantitative result obtained is called its hardness without regard to any relationship between this result and the resistance of the metal to scratching, abrasion, or cutting. It so happens that all that is commonly implied by the term hardness is not susceptible to simple measurement, and consequently measurements are made of quantities that evidently have something to do with it, and these are called hardness values.

As the forcing of a ball, cone, or pyramid into a metal involves deformation of the metal, penetration hardness tests are related to tensile and compression tests in which deformation is also involved. The initial resistance of a metal to deformation is given by its apparent elastic limit, but this does not arise in connexion with hardness tests which always deform the metal beyond it. Under these conditions the behaviour of the metal depends on the rate of strain-hardening, i.e. on the rate at which resistance to deformation increases with deformation. The ultimate tensile stress depends on this property and so does penetration hardness, but owing to the great difference between the two kinds of tests there is no direct relationship between them. For any given class of material an empirical relationship between ultimate tensile stress and penetration hardness as measured in a certain way may be discovered, but the relations established for one material do not apply to the others.

In a tensile test a stress-strain curve may be determined. If the stress is calculated by dividing the load by the original cross-sectional area and the strain determined by measuring the extension between two gauge marks, a curve like those shown in Figs. 27 and 32 is obtained. If, however, the stress is calculated by dividing the load by the actual cross-sectional area at each stage in the test, and the strain obtained from the change in cross-sectional area, a curve like that shown at *A* (Fig. 29) results. In hardness tests the area over which the load is spread increases as penetration proceeds and the conditions are therefore different from those realized in either of the above forms of the tensile test. Nevertheless, the results obtained are ultimately related to the curve shown in Fig. 29, i.e. they depend on the fact that the resistance to deformation increases as deformation proceeds and on the fact that the rate of this increase is at first rapid and later becomes more slow.

Hardness tests were originally introduced in order to investigate the

physical condition of armour plate, steel rails, locomotive tyres, and other products in which hardness is an essential property. Specimens for these tests are easy to prepare and when necessary they may be performed on finished products. Furthermore, the tests are easy to carry out and can be performed rapidly. Apart altogether from their relation to hardness as ordinarily meant they measure certain aspects of the behaviour of metals when deformed. This gives an indication of their general mechanical properties, and any variation in composition or treatment that affects these will also influence hardness. Thus, hardness tests are now applied generally as a check on the condition of metals whether the degree of hardness is important in practice or not. The whole question of hardness tests is considered by O'Neill in *The Hardness of Metals and its Measurement* (120) and only a brief description of them will be included here.

The Brinell Hardness Test.

The best-known hardness test is that invented by Brinell, and until recently it was almost universally used. It is now being replaced to a considerable extent by other methods which are, in general, improved forms of it. In this test a hardened steel ball is pressed into the metal under test by a static load acting for a definite length of time, usually 15 seconds. The size of the impression produced by a given ball under a given load depends on the resistance to penetration of the metal under test. The load in kilograms divided by the spherical area of the indentation in sq. mm. is known as the Brinell Hardness Number, HB. The spherical area of the indentation is calculated from the diameter which is measured by means of a microscope after the load has been removed. For accurate results the surface of the specimen should be polished, the centre of the impression should be more than $2\frac{1}{2}$ times its diameter from the edge of the specimen, the thickness of which should be more than 7 times the depth of the impression.

In practice the Brinell hardness test has been widely used as an empirical test that measures some quantity which gives an indication of certain physical attributes of the metal, and enables different metals to be compared. The fundamental meaning of the test has been the subject of numerous investigations. When all the factors involved are considered, this test is actually more complex than the tensile test, and although it is easy to perform, its significance is difficult to interpret. From a practical point of view one very important feature of it is the relation between the Brinell hardness and the maximum tensile strength of metals. Various values of the ratio between these two quantities have been obtained empirically by different workers, but the most accurate values for steel appear to be those obtained by Greaves and Jones (121) from the analysis of a very large number of test results. The ratios of maximum tensile strength to Brinell hardness number obtained by these investigators are as follows:

Heat-treated alloy steels HB 250-400	0.21
„ „ carbon and alloy steels HB under 250	0.215
Medium Carbon Steel. Annealed or Normalized	0.22
Mild Steel. Annealed or Normalized	0.23

The phenomena which occur when a steel ball is pressed into a flat piece of metal have been studied by many investigators, and most of the information relating to the fundamental aspects of the test has been reviewed and considered by O'Neill (120). The principal features of the process may be stated briefly as follows:

When the ball is pressed into the metal, deformation of both ball and test specimen takes place. As the deformation of the ball is not taken into account in the test, the results are not accurate unless there is a great difference in hardness between the test specimen and the ball, which is made of quenched high carbon or alloy steel, and sometimes further hardened by cold-working the surface. Such balls give accurate results so long as the metal under test does not have a Brinell hardness number above about 450. If it is greater than this, the ball must be changed frequently, and the results obtained on hardened steel cannot be assumed to be strictly comparable with those obtained on softer metals.

The superficial area of the indentation is calculated from the diameter which is measured with a microscope after the test specimen has been removed from the machine. What is actually measured is the diameter of the permanent indentation after elastic recovery has taken place. In soft metals the amount of recovery is small in comparison with the amount of permanent deformation and is therefore unimportant, but in hard metals the elastic deformation represents an appreciable proportion of the whole. There is therefore a considerable difference in the significance of the test as applied to soft and hard metals. In the former case, the size of the impression after the ball has been withdrawn is approximately the same as that produced by the ball, and the result is a fairly accurate measurement of the resistance of the material to deformation. In the latter case, the impression contracts when the load is removed and the result is in reality a measurement of the resistance of the metal to permanent deformation. If the Brinell test is applied to substances other than metal, e.g. rubber, the method appears unsuitable, for in this substance there is a great difference between resistance to deformation and resistance to permanent deformation. In metals, however, there is a more or less constant relation between these properties, and although the Brinell hardness of hard metals is considerably reduced when the diameter of the impression is measured while the load is applied, the relative hardness of different metals is not greatly affected.

The radius of curvature of Brinell impressions in hard metals is different from that of the unloaded ball, and this is attributable partly to distortion of the ball and partly to the fact that elastic recovery of the impression takes place in such a way that its depth decreases more than its diameter. This is known as the 'shallowing effect', the theoretical

explanation of which has been developed by Innes (122). As a result of this the radius of curvature of the permanent indentation is less than that of the ball, and the impression is therefore shallower than would be calculated from its diameter. As the difference between the real depth and the calculated depth increases with the hardness of the metal, there is, in hard metals, a large difference between the hardness number calculated from measurement of the diameter of the impression and that calculated from measurement of the depth.

One of the most important features of the Brinell test is the relation between the diameter of the ball and the applied load. If the applied load were sufficiently small the metal under test might not be deformed beyond its elastic limit, no permanent deformation would then be produced and the metal would appear infinitely hard. Under such conditions the Brinell test would be useless, and the load must therefore be great enough to produce permanent deformation of the metal. Even when this condition is realized, however, the hardness number is different for different loads and ball diameters. This is due partly to the spherical shape of the indenter and partly to the nature of the plastic deformation. When a ball of given diameter is pressed into a given metal, the depth to which it is immersed increases with the load, and as the ball penetrates the metal the angle of indentation changes so that the conditions are not the same for deep and shallow impressions. At the same time, the resistance of the metal increases with the amount of deformation. For these and other reasons the Brinell hardness number obtained with a ball of given diameter varies with the load, and with a given load it varies with the diameter of the ball. The exact conditions that arise when different balls and loads are used cannot be dealt with here and reference to them must be made in the original papers by Meyer (123), Hoyt (124), and O'Neill (125).

As the Brinell hardness of a given metal varies with the load and the ball diameter, it is obvious that the number obtained when a metal is indented under given conditions cannot be regarded as a fundamental property, nor can the results obtained under different conditions be compared. These considerations have led to the standardization of the test conditions, and for steel it is customary to use a ball of 10 mm. diameter and a load of 3,000 kg., while for softer metals a load of 500 kg. is used. It was shown by Meyer, however, that if the test load is adjusted so that the ratio of the load to the square of the diameter is kept constant, comparable results may be obtained with balls of different diameters. With a ball of 10 mm. diameter and a load of 3,000 kg. $L/D^2 = 30$, and when necessary, balls of 1, 2, or 5 mm. diameter may be used with loads of 30, 120, or 750 kg.

The Rockwell Hardness Test.

The Rockwell Hardness Tester is one of a number of machines that have been devised to give direct readings of hardness and thus to avoid

the operation of measuring the diameter of the impression with a microscope. In this machine either a diamond cone or a hard steel ball may be used. The results obtained with the ball are known as Rockwell Hardness 'B', while those obtained with the diamond cone are known as Rockwell Hardness 'C'. The indenter is first applied to the surface of the metal under a definite light load, which is then increased to the specified indentation load, i.e. 100 kg. for the $\frac{1}{8}$ -inch diameter ball and 150 kg. for the diamond cone. The difference between the depth of the indentation under the two loads is the Rockwell hardness, which is read directly on a dial. This test can be performed much more quickly than the Brinell test, and by means of an empirical formula the result can be converted to equivalent Brinell Hardness Numbers with considerable accuracy.

Other Hardness Tests.

Besides the above, numerous other machines have been invented for the determination of indentation hardness. Many of these are of recent origin and consequently have not been widely used. Because of its convenience the Rockwell test has replaced the Brinell test to a large extent in America, but in general there is reluctance to adopt new methods of testing, which, despite their greater convenience, reliability, or theoretical justification, nevertheless give results that are not strictly comparable with those of the machines already in general use.

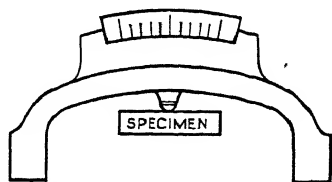


FIG. 185. Diagrammatic sketch of the Herbert pendulum hardness tester.

Among the recently devised hardness testers may be mentioned the Vickers Diamond Pyramid Hardness Tester in which the indentation is made with a diamond pyramid and measured with a microscope, the Shore 'Monotron', in which the load necessary to immerse a 0.75 mm. diamond hemisphere in the specimen to a depth of 0.045 mm. is taken as a measurement of the hardness, and a somewhat similar machine designed by O'Neill (126). The Herbert 'Pendulum' Machine involves quite different principles from any of the others. It consists, as shown in Fig. 185, of a rocker, shaped like an inverted U and supported on a central pivot which carries a 1 mm. steel ball at its point. A curved bubble tube and scale are mounted on top of the rocker. The surface to be tested is polished and set exactly level. The pendulum is placed on the surface and given a specified swing to one side, it is then released and allowed to swing over to the other side. The position of the bubble at the end of the swing is taken as a measurement of the hardness. The mathematics of this method of hardness testing have been explained by Timoshenko (127). Another hardness tester of unique design is the Shore 'Scleroscope' which is a dynamic indentation

hardness tester. In this machine a small hammer with a diamond point falls from a height of 10 inches on to the surface to be tested and then rebounds. The hammer moves inside a graduated glass-tube and the height of the rebound, measured on the scale on the tube, is taken as the Scleroscope Hardness.

NOTCHED-BAR IMPACT TESTS

Several methods of testing notched specimens by impact have been devised, but two methods are now practically standardized, viz. the Izod and the Charpy tests. The former is used in Britain, the latter on the Continent and both are used in America. In the Izod test the specimen is a cantilever held upright in a vice. It is fractured by a blow from a striker which is attached to a pendulum. The standard specimen is 10 mm. square by 75 mm. long. A V-shaped notch with an included angle of 45° , a depth of 2 mm., and a root radius of 0.25 mm., is made at a distance of 28 mm. from one end. The specimen is placed in the vice so that the root of the notch is level with the top of the jaws. The end of the specimen projects 28 mm. above the vice and the point of impingement of the striker is 22 mm. above the notch. In the Charpy test the specimen is a beam 10 mm. square by 60 mm. long. It is notched in the middle

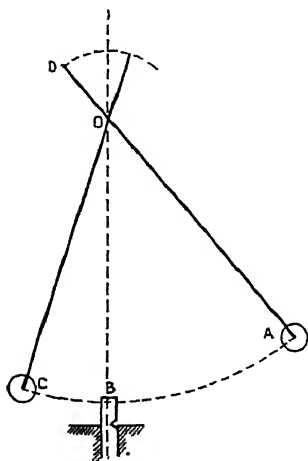


FIG. 186. Diagrammatic sketch of the Izod notched-bar test.

of its length and supported horizontally so that there is a clear span of 40 mm. The notch is made by drilling a hole 1.35 mm. diameter right through the specimen. This hole is then connected to the surface of the specimen by a saw cut. The total depth of the notch is half the thickness of the specimen, and the point of impingement of the striker is immediately behind the notch. As the Izod notch is easier to make it is frequently used in beam tests of the Charpy type.

In notched bar tests made in either the Izod or Charpy machine the quantity measured is the total energy required to fracture the specimen. The pendulum carrying the striker swings about a point vertically above the specimen as shown in Fig. 186. The pendulum is raised to position A and allowed to swing. As it passes B it breaks the specimen and continues to swing to C. Knowing the weight of the pendulum and the difference in height between A and C the energy expended in breaking the specimen can be calculated. In the usual type of impact-testing machine the arm OD moves a loose pointer which shows on a dial the energy expended in ft. lb.

Three characteristics of the Izod and Charpy tests may be noted: (1) the stress applied is a bending stress, (2) the specimen is notched, and (3) the stress is applied suddenly. The general object of the tests is to measure the resistance of the metal to deformation and fracture when subjected to flexural impact at a point where a large local concentration of stress results from a sudden change in section. The notch and the flexural stress are essential features of the test, but there is less certainty about the importance of the velocity of impact. On the one hand, Charpy and Cornu-Thenard (128) and Körber and Storp (129) found that the striking velocity was without appreciable effect, while on the other hand Hadfield and Main (130) and Yamada (131) found that the energy expended in causing fracture varied with the striking velocity. This factor was also studied by Stanton and Batson (132) and some results obtained by them are given in Table 29. From these it will be seen that whereas with some materials the energy absorbed is unaffected by the speed of impact in others it either increases or decreases as the speed increases. The object of the test is to ascertain whether a metal is brittle, i.e. fractures easily, or tough, i.e. fractures with difficulty under the conditions of the test, and several investigators, e.g. Stanton and Bairstow (133), Philpot (134), and Hallam and Southwell (135), have shown that the distinction can be made by means of a slow bend test just as effectively as by an impact test. The energy absorbed in the static test is generally less than in the impact test but the differences between certain materials are just as clearly shown. This does not hold for all materials, however, and Hadfield and Main have shown that with an embrittled mild steel 74.5 lb. may be absorbed in causing fracture in a slow bend test while

TABLE 29

Effect of Variation in Striking Velocity

<i>Material</i>	<i>Energy absorbed</i>		<i>Angle of fracture</i>	<i>Striking velocity</i>	
	<i>Kg.-m.</i>	<i>Ft.-lb.</i>		<i>Metres/sec.</i>	<i>Ft./sec.</i>
0.19% carbon steel	4.03	29.1	5½	2.7	9
	3.83	27.7	3½	4.9	16
	2.77	20.0	3	6.1	20
	2.00	14.5	2	8.8	29
	2.90	20.9	..	4.9	16
Yorkshire iron	2.80	20.2	..	6.6	21½
	1.47	10.6	..	13.1	43
	4.00	28.9	4½	2.7	9
Nickel-chrome steel	4.40	31.8	5	4.9	16
	5.44	39.3	7	13.1	43
	2.66	19.2	2	2.7	9
Embrittled steel, 0.12% carbon	2.30	16.6	1½	4.6	15
	1.19	8.6	½	13.1	43
	1.03	7.5	6	2.7	9
0.65% carbon steel	1.05	7.6	5½	6.1	20
	1.05	7.6	5	13.1	43

only 10.8 lb. are absorbed in an impact test. Furthermore, Yamada has shown that the appearance of low temperature brittleness is detected at a higher temperature in the impact than in the slow bend test.

In view of the fact that in general a similar amount of energy is absorbed in producing fracture by slow bending as by impact, it is worth while to point out that this does not mean that impact does not arise in connexion with metals. It is one of the fundamental facts of mechanics that a live load produces twice the stress of the same load applied gradually. The live load produces an inertia effect and before it is stopped the stress rises as stated. Thus the effect of an impact is out of proportion to the weight of the moving body. This aspect does not arise, however, when the energy expended in producing fracture is measured, and it is for this reason that the comparison of impact and slow bending tests leads in general to a result that is at first sight surprising.

In spite of the fact that brittle materials exhibit a marked difference in behaviour in impact and slow bending tests respectively, it is now generally considered that the essential features of the tests are the notch and the flexural stress, and in consequence the test is sometimes termed the notch-bar bending instead of the notched-bar impact test. In performing the test the form of the notch must be carefully standardized, for the results are affected by its depth and angle and to a most pronounced extent by the sharpness of the root. It is usual also to standardize the dimensions of the specimens and to quote the results in terms of the energy required to fracture a standard specimen. Several investigations have been carried out to discover whether there are any fixed relations between the energy absorbed and the dimensions of the test-piece, for if such could be established it would then be possible to express results in a form that would enable specimens of different sizes to be compared. No such relations have yet been definitely established and it is therefore customary to adhere to the standard conditions in all tests.

Notched-bar tests have been the subject of much controversy and it is therefore worth while to consider their significance from the point of view of the objects of testing stated at the beginning of this chapter. It is there pointed out that a test may be useful because (1) it determines the behaviour of the metal under conditions similar to those realized in service, (2) it measures some quantity that is related to the fundamental mechanical properties of the metal, or (3) it is a good indication of whether a given consignment of metal is similar to that used successfully before. As already stated, the immediate object of the test is to measure the resistance to fracture when subjected to flexural impact at a point where a large local concentration of stress results from a sudden change in section. In modern engineering practice there are many parts of intricate shape with sudden changes in cross-section, and when such parts are subjected to sudden or impact loading, con-

centrated stresses of high and generally unpredictable magnitude occur in the region of the change in section. In such a case the result obtained in an Izod test might be expected to have a direct bearing on behaviour in service. A characteristic of the test, however, is that the applied force is more than sufficient to break the specimen or bend it out of the way of the striker, whereas in service such a force is not likely to be applied unless an accident occurs. Service failures are more generally due to the repeated applications of a stress, and the important question is whether the results obtained in single-blow impact tests have a direct connexion with behaviour under repeated small blows. The available evidence indicates that when numerous light blows are applied, the behaviour of notched specimens is related to their endurance limit, which may have little connexion with their resistance to a single blow. Thus the Izod test does not directly indicate resistance to repeated impact when a large number of light blows are concerned; it does, however, indicate resistance to one heavy blow and to a small number of comparatively heavy blows. In all cases of repeated stress where tension, bending, or torsion is involved the endurance of a metal is reduced by changes in section and surface irregularities. These surface effects become more pronounced as the hardness of the metal increases and as the Izod value decreases. Thus although the Izod test does not imitate service conditions, and although the resistance of smooth polished specimens to repeated stress is not related to their notch-toughness, yet the endurance of metals with a high-notch toughness is reduced to a less extent by changes in section and surface irregularities than that of metals with low notch-toughness.

It is with respect to the direct connexion between Izod tests and service conditions that the most uncertainty prevails. Its usefulness in other respects is more apparent, and we may now consider it as a method of measuring some quantity connected with the fundamental mechanical properties of the metal. These are in general the properties that determine the relations between stress on the one hand and deformation and fracture on the other, and these are discussed in Chapter III. Briefly, if we arrange a series of metals in order of increasing resistance to deformation we find the following transitions in other properties. Beginning with metals like tin and lead we find low ultimate tensile strength and hardness, high elongation, and reduction in area. These are the soft and plastic metals, and while they can be bent with ease through 180° they exhibit no tendency to fracture. Passing to metals like pure copper, aluminium, iron, and nickel, or alloys like brass, mild steel, and cupro-nickel, we find increased tensile strength and hardness, elongation slightly less than in the above metals, and reduction in area considerably less. These are the ductile metals and they may also be bent through 180° without breaking, but a greater force is required to do this. When greater resistance to deformation is needed, i.e. when higher tensile strengths are required, steels of higher carbon

content or quenched and tempered carbon or alloy steels are used. In these materials the elongation and reduction in area decrease as the strength and hardness increase and the general character of the metal changes from ductile to tough. Such a metal has a high tensile strength and hardness and a moderate to low elongation and reduction in area. It requires a great force to bend it and it may break before it has been bent through 180° . On further increasing resistance to deformation as e.g. by using steels tempered at lower temperatures, the tough begins to pass into the brittle condition. This transition is marked by a further decrease in elongation and reduction in area, and at first the strength and hardness may continue to rise, but a bending force will tend to produce fracture rather than deformation, and its magnitude will be less than that required to bend the tough material. On further increasing the resistance to deformation the strength will begin to fall with the elongation and reduction in area and the brittleness of the metal will be revealed in the tensile test. The hardness, however, will continue to increase.

The effect of a gradual change in the properties of a metal on the values obtained in the tensile and hardness tests is illustrated in Figs. 527 to 529, Chapter XV. These figures show that at about 30–35 per cent. of zinc the copper-zinc alloys begin to change from the ductile to the tough condition, i.e. the strength and hardness begin to rise rapidly while the elongation begins to fall. Between 45 and 50 per cent. of zinc the alloys change from the tough to the brittle condition, i.e. the strength falls with the elongation while the hardness continues to rise. In metals intended for cold-working operations the capacity for deformation as indicated by elongation and reduction in area is of direct importance, but in metals prepared for use it is resistance to and not capacity for deformation that is of direct importance. This resistance is shown in the first instance by the yield-point or the proof-stress, but it is also indicated by the ultimate tensile stress, for if a metal has a low resistance to deformation it cannot have a high tensile strength. In use, however, resistance to fracture is also important, and whereas some indication of this is given by the ultimate tensile strength it does not give all the information required. If a metal has a high hardness, and low tensile strength, elongation, and reduction in area, it is shown to be brittle in the tensile test. If, however, the tensile strength is high and the elongation moderate the tensile test indicates toughness. But the test does not imitate service conditions, and under the varied circumstances in which a metal is employed it may be found to fracture easily as a result of its inability to distribute stress concentrations arising at changes in section and surface irregularities. Increased ductility counteracts this tendency to fracture easily under conditions different from those realized in the tensile test, and it is for this reason that elongation and reduction in area are important. Taken in conjunction with the tensile strength they indicate resistance to

fracture. Even this is not conclusive, however, for a metal in which the proof-stress (or yield-point) and ultimate tensile strength indicate a satisfactory resistance to deformation, and in which the elongation and reduction in area show a sufficient capacity to resist fracture under varied conditions, may yet fracture with unexpected ease in service. This is most likely to occur when the elongation and reduction in area have been allowed to drop to a comparatively low value in order to secure a high tensile strength and yield-point, i.e. when the metal is tough from the point of view of the tensile test, and it is in these circumstances that the notched-bar test is most generally employed. It may also occur, however, even when the metal is ductile as shown in the tensile test, and in the case of metals that may behave in this way and are to be used where a high resistance to fracture is essential the notched-bar test may again be employed.

In the tensile test the conditions tend to produce deformation rather than fracture, and unless the metal is very brittle it does not break until the tensile stress on the reduced cross-sectional area has reached a high value. The hardness test is even more favourable to the production of deformation rather than fracture. In the notched-bar test, however, the conditions favour fracture which can take place easily by the propagation of a crack from the root of the notch. The test is thus a sensitive method of detecting a tendency to fracture rather than deform and it shows degrees of brittleness not revealed in the tensile test. When a metal specimen held in the vice of an Izod machine (Fig. 186) is struck, it has three alternatives: (1) it may fracture, (2) it may bend out of the way of the striker, or (3) it may bring the striker to rest before either of the other results has been realized. If the striker is brought to rest no quantitative result is obtained, but it is shown that the test-piece is beyond the capacity of the machine. With the standard Izod specimen and the standard machine which gives a blow of 120 ft.-lb. this circumstance rarely arises. We may therefore confine our attention to the first two alternatives and their combinations. If the metal under test is very ductile the tendency to deform is great, and when it is struck it bends readily and a considerable amount of energy is expended in deforming it. Thus steels containing less than 0.2 per cent. of carbon frequently bend clear of the striker without fracturing. At the other extreme steels hardened by quenching fracture without appreciable distortion. In general, however, bending and cracking take place simultaneously and fracture occurs after a certain amount of distortion. The energy absorbed in breaking the specimen is made up of that expended in deformation and that used in initiating and propagating the crack. As the former is of greater magnitude than the latter the energy absorbed is related to the extent to which the specimen is bent. It will thus be seen that in one blow the notched-bar test gives a value that is related to the capacity of the metal to resist deformation or fracture, or both. This is illustrated in Table 30 where the mechanical properties of a

series of representative materials are given. These values should not be taken as indicating the specific properties of the materials mentioned, for in each metal the mechanical properties may vary considerably with variations in composition and in heat and mechanical treatment (Parts V and VI). The figures do represent, however, the general

TABLE 30

Some Mechanical Properties of Various Metals

<i>Metal and treatment</i>	<i>Tensile strength tons/sq. in.</i>	<i>Elongation % on 2 in.</i>	<i>Reduction in area %</i>	<i>Brinell hardness</i>	<i>Izod ft.-lb.</i>
Water-quenched carbon steel . . .	50	0	0	700	0
Oil-quenched alloy steel . . .	119	10	21	572	7
Oil-quenched and tempered alloy steel . . .	61	23	60	290	64
Water-quenched and tempered carbon steel . . .	49	28	66	228	94
Hot-rolled Monel metal . . .	38	40	55	160	115
Commercial nickel . . .	31	47	70	85	110
Pure iron . . .	17	48	70	67	80
Pure copper . . .	14	54	75	44	45
Pure aluminium . . .	5	60	95	16	..

relations between the measurements made in the tensile, hardness, and notched-bar tests. The metals are arranged in order of increasing ductility and it will be seen that the hardness is a maximum when the ductility is nil, that the tensile strength is a maximum when the ductility is small, and that the notched-bar value is a maximum when the ductility is considerable, e.g. in Monel metal. Down to Monel metal and nickel the notched-bar value increases because the resistance to fracture increases while the resistance to bending decreases. Below this, i.e. in iron and copper, the notched-bar value decreases with the resistance to bending.

The above discussion is designed to show that the results obtained in notched-bar tests are in general related to the fundamental properties of the metal, i.e. they depend to some extent on the relations between stress, deformation, and fracture. As far as design, specification, and acceptance testing are concerned, elongation and reduction in area are used to ensure that a high strength has not been obtained by sacrificing the ability of the material to resist fracture by distributing stress concentration. Notched-bar values may be used for the same purpose. In steels, however, variations in composition and treatment frequently lead to variations in notched-bar values that are not related to changes

in other properties. This is a common occurrence in mild steel and also in many quenched and tempered alloy steels. These latter exhibit a phenomenon known as 'temper-brittleness'. All steels in the hardened condition have a low elongation, reduction in area, and notched-bar value. On tempering at progressively higher temperatures the elongation and reduction in area increase with the tempering temperature, but in steels that are susceptible to temper-brittleness the Izod value does not change in this simple way. Tempering at temperatures below 200° C. results in an increase in the Izod value which rises to a maximum at 200° C. On raising the tempering temperature the Izod value begins to decrease and reaches a minimum between 300° and 400° C. The effect of higher tempering temperatures depends on the rate of cooling after tempering. If the steel is quenched from tempering temperatures above 450° C. the Izod value rises with the tempering temperature. If it is slowly cooled the Izod remains low. Thus, if two specimens of the same steel are subjected to the same treatments at all stages except that after tempering at 600–650° C. one is quenched while the other is slowly cooled, then the former will have a high Izod value while the latter will have a low one. This is shown by the following figures:

Effect of Tempering Temperatures and Rate of Cooling on Izod Values

Tempering temperatures	Izod value, ft.-lb.	
	Water quenched	Air cooled
..	9	9
100° C.	11	11
200° C.	17	17
300° C.	9	9
400° C.	8	8
550° C.	30	7
600° C.	41	8
650° C.	53	8

The phenomenon of temper brittleness is further considered in Part V. For the time being it is sufficient to point out that in a wide range of alloy steels the tempering temperature and the rate of cooling after tempering have a pronounced effect on the notched-bar value. If, e.g., a specimen of one of these steels is tempered at 600° C. and cooled slowly instead of rapidly, its Izod value will be very low while its other mechanical properties will be unaffected. Furthermore, if it is tempered below 500° C. in order to obtain increased tensile strength, its Izod value will be low in whatever way it is cooled. The steels that are susceptible to temper brittleness are the metals most widely used where high strength is required and the most rigorous testing is therefore necessary. The examination of service failures has provided evidence which indicates that when the other properties are similar, components that have been treated so as to give a low Izod value break more readily than those that have a high Izod value. Consequently, an Izod test is usually

specified in connexion with steels of this kind and this is the principal use of the test.

The application of the Izod test to heat-treated alloy steels rests on the third reason for testing, i.e. it indicates whether a given consignment of metal is similar to that used successfully before. In practice this is its principal application. For purposes where high strength is required only alloy steels are available, and theoretical consideration combined with experience indicate that the best performance in service will be obtained if the necessary strength is associated with a high Izod value. A minimum Izod value is therefore specified in order to ensure that the steel has been given the requisite treatment. In these metals pronounced variations in notched-bar toughness may occur while the other mechanical properties remain unaltered, and the use of the Izod test in this connexion means no more than that a high Izod value is considered to be more satisfactory than a low one. Little justification has yet been found for attaching a wider practical significance to the test. Thus, little account of Izod values is taken in comparing the merits of aluminium alloys and steel unless the component is notched, and in general such tests are not specified except in connexion with alloy steels. The fact that the Izod test in general measures something that is related to the fundamental mechanical properties of the metal does not necessarily justify its wide use as an acceptance test, for the quantity that it measures may not be of general importance in service, and furthermore, it is in many cases related to the combined values of tensile strength and elongation.

CREEP AND CREEP TESTS

In the methods of testing so far described the results are obtained in a short time and with one application of stress. In order to determine the behaviour of metals when subjected to prolonged loading or the repeated application of a range of stress other methods of testing are required. This gives rise to creep and endurance testing. Such tests when scientifically conducted take a long time to perform and are employed for purposes of investigation rather than for routine testing. They are used in the first place to study the behaviour of metals when subjected to prolonged or repeated stressing and to discover the effect of such factors as the condition of the metal surface, &c. They are also used to compare the resistance of different metals to prolonged or repeated stressing and to find the effect of composition and treatment on this resistance. In this way the relative suitability of different metals for applications where prolonged or repeated stress will be applied is ascertained and metals are selected for service trials. When these prove satisfactory a specification is drawn up with the object of ensuring that further supplies will resemble the metal tested and tried. This can be done by stating the composition and treatment required and by specifying

ing a particular performance in tensile, hardness, and notched-bar tests. Thus although creep and endurance tests are not used for acceptance purposes, they have a close relation to such tests.

Creep is continuous deformation with time under a constant load and is therefore one aspect of the relations between stress, time, and temperature on the one hand and deformation and fracture on the other. These relations are considered in Chapter IV. Creep may result from any type of static stress, e.g. tension, torsion, shear, or bending, but most of the investigations on the subject have been devoted to the study of creep in tension. It may occur in most of the common metals at atmospheric temperature. In iron and steel it is unimportant at this temperature because it only occurs to a very small extent. In copper and aluminium it occurs to a greater extent and under smaller stresses, but interest mainly attaches to the conditions under which it proceeds to a marked extent under stresses considerably less than the ultimate tensile stress. These conditions are realized with lead, tin, and zinc at atmospheric temperature, with aluminium and copper at somewhat higher temperatures and with iron and nickel at temperatures above 350–400° C. In general, alloys have a greater resistance to creep than the metals on which they are based and some alloys based on nickel and iron are so resistant that they are suitable for use at temperatures above 900° C.

When the whole range of materials from the heat-resisting alloys based on iron and nickel to the pure metals, lead and tin, is taken into account, extensive variations in the relations between creep, stress, and temperature are encountered. Thus the behaviour of heat-resisting steels and nickel alloys above 900° C. resembles that of lead at atmospheric temperature, and between these extremes lie all the other metals and alloys, e.g. ordinary steels, copper alloys, and aluminium alloys. In each metal or alloy creep will take place if it is subjected to stress while maintained above a certain minimum temperature. Each metal or alloy has therefore a creep range, but the general behaviour of all metals in the appropriate ranges of temperature is fundamentally the same. The purpose of the present discussion is to explain the general features of creep phenomena and it might lead to some confusion if an attempt were made to keep all metals in mind while dealing with these. Most of the investigations on the subject have been concerned with steel, and in the discussion that follows this metal will be considered. In general, the behaviour of ordinary varieties of steel at temperatures in the range between 300–600° C. is the same as that of heat-resisting alloys at higher temperatures and of other alloys at lower temperatures. There is, however, one respect in which steel differs from many other alloys, viz. in its capacity for strain-ageing, and in what follows it must be remembered that the effects attributed to this phenomenon will be less pronounced and even absent when metals other than steel are concerned.

The phenomena on which creep is essentially based are described at the beginning of Chapter IV. It is there explained that when a test-bar is continuously deformed by a tensile load its resistance to deformation when considered as a whole first increases and then decreases. Consequently when the load (or the stress per unit of original area) is plotted against extension, curves like those shown in Figs. 27 and 32 (Chapter III) are obtained. It is then explained that under a constant load less than the ultimate tensile stress deformation may proceed with time although the resistance to deformation is increasing. Under these conditions, however, the amount of deformation taking place in successive equal time intervals decreases as the total time under load increases, and as the rate of deformation becomes very small it eventually appears to stop at a point that depends on the sensitivity of the apparatus used to measure it. The curve connecting time and deformation has the form shown in Fig. 66, and the shape of this curve, combined with the results obtained when the load is increased after the metal has been subjected to a constant load for some time (Fig. 67), shows that deformation may continue under a constant load while resistance to it is increasing.

The ultimate tensile stress is the point at which resistance to deformation is a maximum and further deformation is accompanied by decreasing resistance. Thus, if a load equal to the ultimate tensile stress is applied, the metal will continue to deform until fracture occurs and in this case the deformation proceeds at an increasing rate. It is shown at the beginning of Chapter IV that metals can deform under constant loads while the resistance to deformation is either increasing or decreasing, and the two cases are distinguished by the fact that in the former the rate of deformation decreases with time whereas in the latter it increases with time. The next step in the argument developed in Chapter IV was to show that under a constant load the point of maximum resistance to deformation may be passed, so that after proceeding for some time at a decreasing rate deformation may begin to proceed at an increasing rate. This conclusion follows from the fact that the point of maximum resistance to deformation depends both on stress and time. Under the conditions realized in a short-time tensile test the point of maximum resistance to deformation is the ultimate tensile stress, but as this quantity depends on something that is influenced by time it loses its significance when time is taken into account. It may be said that (neglecting strain-ageing) the ultimate tensile stress occurs at a lower stress after a longer time, but it is best to restrict the use of this term to short-time tests and to speak of the maximum resistance to deformation when taking account of time.

Typical deformation time-curves are shown in Fig. 70. Under constant load deformation first proceeds at a decreasing rate and reaches a minimum at the point of maximum resistance to deformation, after which it proceeds at an increasing rate to fracture. Several conclusions

may be drawn from the general relations between time and deformation illustrated by the curves in Fig. 70. In the first place, it is evident that the amount of deformation produced on the first application of the stress will increase with the magnitude of the stress. In the second place, it is evident that the original rate of deformation will increase with the magnitude of the stress. Furthermore, the time taken to reach the minimum rate of deformation will decrease as the magnitude of the stress increases, and at the same time the rate of deformation at the minimum will increase. At the point of inflexion the rate of creep is neither increasing nor decreasing, but at all other points on the curves in this figure the rate of creep is changing. In practice, however, it will frequently be impossible to detect this change. If, e.g., a specimen is subjected to a stress that produces creep that proceeds at a decreasing rate for a long time, then the rate may eventually become so low as to be incapable of measurement. It may then continue at a decreasing rate for a further time and finally begin to increase again. All this may take place, however, without any measurable change in the length of the specimen, and consequently for some distance on each side of the point of inflexion the curve will be a horizontal line and will not begin to bend upwards until the increasing rate of creep leads to deformation of measurable magnitude. With a given metal under a given load at a given temperature the length of the horizontal portion will increase as the sensitivity of the apparatus used to measure elongation decreases.

It follows from the above that, if a given metal is subjected at a given temperature to constant stresses of different magnitude, a set of curves like those shown in Fig. 85 (Chapter IV) will be obtained. In curves *C*, *D*, *E*, *F*, *G*, the point of inflexion is reached within the time covered by the figure, but in curves *A* and *B* creep is still proceeding at a decreasing rate. From curve *A* to curve *G* the initial deformation increases with the stress and from curve *C* to curve *G* the rate of creep at the point of inflexion increases with the stress. The rate of creep at the point of inflexion on curve *B* would be less than that on curve *C*, but this point has not been reached in the period of the test. Actually, however, the rate of creep on curve *B* at the time when curve *C* reaches its minimum is less than the minimum on curve *C*. In other words, at any instant the rate of creep under lower stresses is less than that under higher stresses whether the minimum rate has been reached or not.

When a metal is deformed at different temperatures the amount of strain-hardening produced by a given amount of deformation decreases as the temperature increases, i.e. the true stress-deformation curve *A* (Fig. 69) becomes less steep. Thus, if a given metal is subjected to the prolonged action of a given stress at a series of temperatures, it will be found that, in the absence of strain-ageing, the initial deformation and original rate of deformation increase with the temperature, while the time taken to reach the minimum rate decreases and the actual rate

at the minimum increases. Consequently, the set of curves shown in Fig. 85 may be taken to represent the effect of the same stress at different temperatures as well as that of different stresses at the same temperature.

In the foregoing discussion of the relations between stress, time, and temperature, the effect of the changes that follow deformation has not been taken into account. As explained in the section dealing with these changes (Chapter IV), strain-ageing denotes an increase in resistance to deformation that takes place after deformation, while recrystallization denotes a decrease in resistance to deformation whether the appearance of new crystals is microscopically evident or not. Both these changes and the relations between them are affected by time, temperature, amount of deformation, and the nature and condition of the metal concerned, and the subject is fully considered in the above chapter. For the present purpose, however, all that has to be taken into account is the effect of those changes on creep. It is obvious that strain-ageing will tend to increase the resistance to creep while recrystallization will tend to decrease it. In the case of a metal creeping at a decreasing rate it is impossible to determine whether the decrease is due to the direct relations between time and deformation, to strain-ageing, or to the combined effect of both, unless the metal can be shown by other means to be incapable of strain-ageing. In some cases it is equally impossible to determine whether creep at an increasing rate is due to the relations between time and deformation, to recrystallization or to both, but in others recrystallization may be shown to be in operation by studying the changes in microstructure. While the effect of these changes on creep cannot be ignored, the view adopted in this book is that the characteristic form of the deformation-time curves for tensile stresses is determined by the relations between time and deformation, and that the changes that follow deformation simply have the effect of modifying these relations. Thus strain-ageing increases the resistance to deformation and consequently increases the stress, temperature, or time necessary to attain the point at which deformation at an increasing rate begins, while recrystallization decreases resistance to deformation and thus reduces the stress, temperature, or time necessary to attain the point at which deformation at an increasing rate begins. The characteristic of deformation in tension is that the cross-sectional area decreases while deformation proceeds, and the relations between strain-hardening and reduction in cross-sectional area give rise to the point of maximum resistance to deformation which is associated with the ultimate tensile strength and the minimum rate of creep. When, however, metals are deformed by compression or bending, the cross-sectional area does not diminish as deformation proceeds and thus resistance to deformation increases progressively and does not pass through a maximum. Under these conditions the rate of deformation under a constant load must decrease progressively and continued

creep must depend on the elimination of strain-hardening and strain-ageing by recrystallization.

It has been suggested that creep can be entirely accounted for in terms of strain-hardening and recrystallization. Thus when a stress is applied, a certain amount of deformation is produced and the metal is strain-hardened to a given extent. If the relations between time and deformation as described above are neglected, it follows that as long as the strain-hardening remains constant or increases as a result of strain-ageing no further deformation should occur. Under suitable conditions of time, temperature, and amount of deformation, recrystallization will sooner or later begin, and then the resistance to deformation will decrease, a further amount will take place and the metal will again be strain-hardened. Eventually this strain-hardening will disappear and further deformation will occur, and thus creep will depend on the balance between strain-hardening and recrystallization. There is no doubt that creep can take place in this way and that in many cases it is an important factor in this change. But creep can also take place when there is no recrystallization, and all the features of the tensile strain-time curves cannot be accounted for in terms of strain-hardening and recrystallization. When creep is proceeding under a tensile stress the cross-section of the specimen is diminishing, and it is clear that so far as the relations between strain-hardening and creep are concerned they can only account for creep at an increasing rate. They cannot account for creep at a decreasing rate nor for the fact that it takes place under conditions which do not permit recrystallization and even produce strain-ageing. Creep takes place in steel at atmospheric temperature, although the metal strain-ages and does not recrystallize at this temperature. At 300° C. it takes place readily, yet Rosenhain and Hanson (136) subjected specimens of steel to loads between one-third and two-thirds of their ultimate tensile strength for $5\frac{1}{4}$ years at this temperature and at the end of this time the specimens were found to have hardened. Furthermore, whereas Carpenter and Smith (108) found that work hardened aluminium retained its increased hardness for 5 years at atmospheric temperature, Welter (137) found that this metal stretched at a decreasing rate for 13 months under a constant stress of 1.08 tons per sq. in. He also found that copper continued to deform for 13 months at air temperature under a stress of 1.21 tons per sq. in., and yet Pilling and Halliwell (65) have shown that the softening of severely worked copper at air temperature is an infinitely slow process if it can be said to take place at all. In short, creep at a decreasing rate can take place when there is no recrystallization and it can also take place at an increasing rate without the intervention of this phenomenon. At the same time, however, creep at an increasing rate is facilitated by recrystallization and in many cases this is the controlling factor. Just as recrystallization tends to increase the rate of creep so strain-ageing tends to decrease it.

Creep and the Limit of Proportionality.

When the steel is to be used at atmospheric temperature the results obtained in short-time tensile tests are sufficient for purposes of design, but when it is subjected in service to temperatures above 300°C . a knowledge of its behaviour in short-time tests at the appropriate temperature is not enough. At stresses far below the ultimate tensile strength it may creep to fracture or until an undesirable amount of deformation has taken place, and it is therefore necessary to know the effect of stresses applied for a long time. As the time for which the steel may be required to maintain its strength in service may be of the order of years, it is impossible to determine directly the stress that it can withstand for this length of time. Consequently, it is necessary to devise methods of testing from which the probable behaviour during long periods may be deduced.

The phenomenon of creep is influenced by (1) the stress required to initiate permanent deformation, (2) the relations between time and deformation, (3) the relations between stress and deformation, (4) strain-ageing, and (5) recrystallization. (2), (3), (4), and (5) have already been considered and it remains to consider (1) from the point of view of its bearing on creep in general, and on possible methods of determining the stress that can be withstood for long periods without appreciable deformation or failure. It should be said in the first place that at temperatures in the creep range steel does not give a short-time stress-strain curve with a large yield-point like that shown in Fig. 32, but gives a smooth curve like that shown in Fig. 27 on which the beginning of permanent deformation is simply marked by the change in slope (if any) at the elastic limit. What has to be considered therefore is the effect of time and temperature on the elastic limit.

When other conditions are the same, the limit of proportionality depends on the accuracy of the instrument used to measure extension. If the extensometer has a sensitivity of 0.00001 inch per inch, i.e. if it can detect an extension of 0.00001 inch multiplied by the gauge length, then as soon as this amount of permanent deformation takes place departure from linearity will be observed. If, however, the sensitivity of the extensometer is only 0.0001 inch per inch, then the departure from linearity must be ten times as great before it is observed. Tapsell (64) gives the figures shown in Table 31 to illustrate the effect of the sensitivity of the extensometer on the limit of proportionality obtained from the load-extension curve of a steel tested at 400°C .

Even with the most sensitive extensometers, however, the limit of proportionality obtained by gradually increasing the load has little significance when the conditions are such that deformation proceeds to an appreciable extent with time. In determining this value it is usual to apply the load in steps and note the extension produced by each increase in load. Each step may occupy one minute, and an extensometer that can detect an extension of 0.0001 inch per inch will not

record the beginning of permanent strain unless it takes place at the rate of 0.0001 inch per inch per minute. In general, the limit of proportionality determined with an extensometer of given sensitivity decreases progressively as the temperature is raised, for this quantity, like the yield-stress, is not affected by strain-ageing, which does not begin until an appreciable amount of permanent deformation has been produced. Furthermore, the limit of proportionality, particularly at temperatures above 300° C., tends to decrease with increase in the time taken in its

TABLE 31

Extensometer Sensitivity and Limit of Proportionality

<i>Sensitivity of extensometer: limit of strain measurement inch per inch</i>	<i>Deduced value of limit of pro- portionality from given stress- strain curve. Tons per sq. inch</i>
0.000002	10.0
0.00001	11.2
0.00002	12.4
0.0001	16.8

determination. A quantity which is expressed in terms of tons per sq. in. and yet depends on the relations between time, temperature, and the sensitivity of the extensometer is not of much significance. It may frequently be found that a metal will withstand for a long time without substantial deformation any stress lower than the limit of proportionality determined with a certain extensometer at the temperature in question, while under appreciably higher stress creep proceeds to a pronounced extent. This result is just a coincidence, however, for had a more sensitive extensometer been used it would have been found that even at stresses above the limit of proportionality the rate of creep was negligible, while had a less sensitive instrument been used it would have been found that creep proceeded at an appreciable rate at stresses below the limit of proportionality. Even when time can be neglected, the limit of proportionality is an indefinite quantity because of its dependence on the extensometer, and when time must be taken into account the measurement becomes more indefinite. Under certain conditions it may be found that the limit of proportionality determined with a given extensometer and rate of loading is an indication of the stress which the metal can withstand at the temperature in question without much deformation, but the relationship is quite empirical and has no fundamental significance.

The determination of the modulus of elasticity at elevated temperatures is affected by the same factors as influence the determination of the limit of proportionality. But owing to the fact that iron, carbon steels, and steels with low contents of alloying elements, have approximately the same modulus over a range of temperature, Tapsell has been able, from data relating to Armco iron and twelve different steels, to draw a

general curve illustrating the decrease in the modulus of elasticity with rising temperature. This curve is shown in Fig. 187.

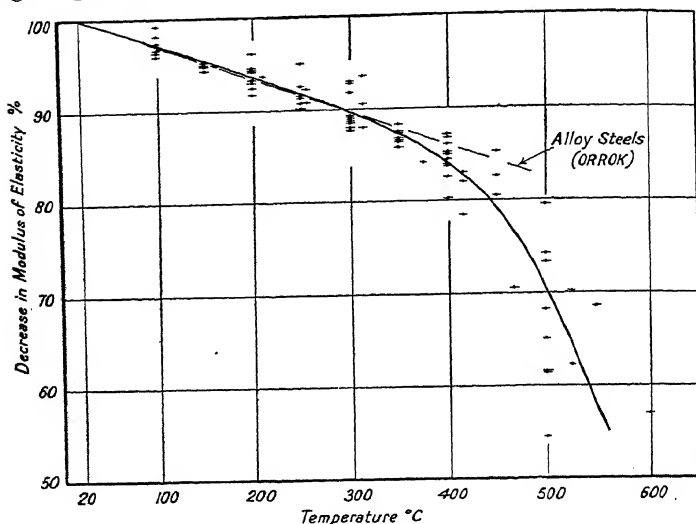


FIG. 187. Decrease in modulus of elasticity with rising temperature. Carbon and low alloy-content steels. (Tapsell, *Creep of Metals*.)

Creep Characteristics of Steel.

It has long been known that the strength of steel and other metals is much reduced at elevated temperatures, but until quite recently it was assumed that this reduction could be measured by means of ordinary short-time tensile tests at these temperatures. The increasing use of high temperatures in internal-combustion engines, high-pressure steam boilers, and turbines using superheated steam, has stimulated interest in the properties of steel at these temperatures, and the importance of the time factor is now realized.

Experimental investigation of the creep of metals is still comparatively new. One of the earliest researches was that by Andrade (138) who experimented with wires of several metals, including iron, copper, and lead, under constant stress. He showed that although there was considerable difference in the behaviour of these metals at any given temperature, they appeared to obey the same general laws of flow when a wide range of temperature was taken into account. Practical interest in creep began, however, with the work of Chevenard (139) in 1919 and Dickenson (140) in 1922, and since then numerous investigators have contributed to the study of the subject. In the early stages of the study of creep the experimental methods used lacked some of the refinements now known to be necessary. Even at the present time there is little standardization of the methods of testing at elevated temperatures, and

the available information relates to experiments carried out with extensometers of different degrees of sensitivity, under different degrees of accuracy of temperature control, and with very different views regarding the length of time necessary to determine creep characteristics.

Practically all the work in the last ten years has been carried out in order to obtain as quickly as possible information for use in design. During that time the demand for metals to withstand higher temperatures has been growing more insistent, and new alloys have continually been produced to meet it. Concurrently with this the creep properties of existing metals have been under investigation, and to a lesser extent new alloys have been studied. The circumstances have not permitted the extensive study of creep in its fundamental aspects, and in the absence of scientific knowledge a great variety of testing methods have been devised. The object of the study of creep is to obtain information regarding the properties of metals when subjected to stress for long times at elevated temperatures so that (1) the stress that a given metal will withstand for a long time may be determined, (2) the suitability of different metals under given conditions may be compared, and (3) the amount of deformation produced by a given load either initially, or after a long time may be measured.

The basis of creep testing is to subject a specimen to a given load at a given temperature and measure its elongation under this load for a certain time. In this way a deformation-time or creep curve is obtained. The value of such a curve depends on the accuracy with which the temperature is controlled and the elongation measured, but it also depends on the length of time during which the behaviour of the metal is observed, and one of the principal differences in the work of different investigators has been in the duration of their tests. Some investigators consider that the necessary information can be obtained from tests of a few hours' duration, others run their tests for some days, while others hold that the minimum time for reliable tests is from 40 to 100 days. There is no doubt that tests of comparatively short duration must be devised for routine use, but the value of these tests can only be ascertained when the phenomenon of creep is understood. For this purpose long-duration tests are necessary, and from a consideration of these it should be possible to discover to what extent short-duration tests can be relied on, and what factors are important in performing them. That a particular empirical test of short duration gives information that enables a metal to be used with safety is no evidence of the value of the test, for metals were used at elevated temperatures without failure, and sometimes without appreciable distortion, when nothing whatever was known of their properties under these conditions. To demonstrate the value of a test it is also necessary to show that it gives information that enables the metal to be used to the best advantage, so that reliability is not obtained by a disproportionate sacrifice of

efficiency. At the present time it is necessary to study the creep characteristics of metals by means of long-duration tests; but when these characteristics are known for a given metal, short-duration tests may be used to ascertain whether a particular consignment is up to standard or not. The most extensive investigations of creep by means of long-duration tests have been carried out at the National Physical Laboratory, Teddington. Numerous reports and papers on the subject have been issued from there, and the whole matter is excellently surveyed in *Creep of Metals*, by H. J. Tapsell (64).

Creep Curves.

Creep curves are obtained by measuring the extension at suitable time-intervals of specimens subjected to a constant load at a constant temperature. In these curves strain (or deformation) is plotted against time. The general form of the curves obtained under different loads at the same temperature, and under the same load at different temperatures, follows directly from what has been said in the previous sections about the relations between stress, time, temperature, and deformation. Fig. 188 shows the short-time tensile stress-strain curve and a series of creep curves for a carbon steel at 300° C. At this temperature considerable strain-hardening and ageing takes place. The limit of proportionality as determined by the tensile test is 12 tons per sq. inch, and under this stress no creep takes place as is shown by the lowest of the creep curves. A stress of 18 tons per sq. inch gives rise to a small initial permanent strain followed by a small amount of creep, which, however, proceeds very slowly and after a few days appears to cease. A stress of 21 tons per sq. inch produces a higher initial strain and creep proceeds more rapidly and continues for a longer time before its rate becomes negligible. Stresses of 24, 27, and 30 tons produce still greater initial strains and creep rates, but under each stress the creep rate continually decreases and finally becomes very small. A stress of 32 tons per sq. inch, however, produces a very rapid initial rate of creep, and although this decreases continuously with time it is still considerable after 85 days, and there is no doubt that the specimen would eventually fracture under this stress. The curve representing the behaviour of the metal under a stress of 34 tons per sq. inch resembles the others in that the creep rate at first decreases. After 35 days, however, the rate having reached a minimum, begins to increase and the specimen was actually broken in 119 days. Under a stress of 36 tons per sq. inch there is no initial decrease in rate, creep begins rapidly and continues until fracture occurs.

Fig. 189 shows the short-time tensile stress-strain curve and a series of creep curves for the same carbon steel at a temperature of 500° C. At this temperature there is little strain-hardening or ageing, and creep proceeds rapidly under very small loads. The limit of proportionality determined from the stress-strain curve is 3 tons per sq. inch, but even under

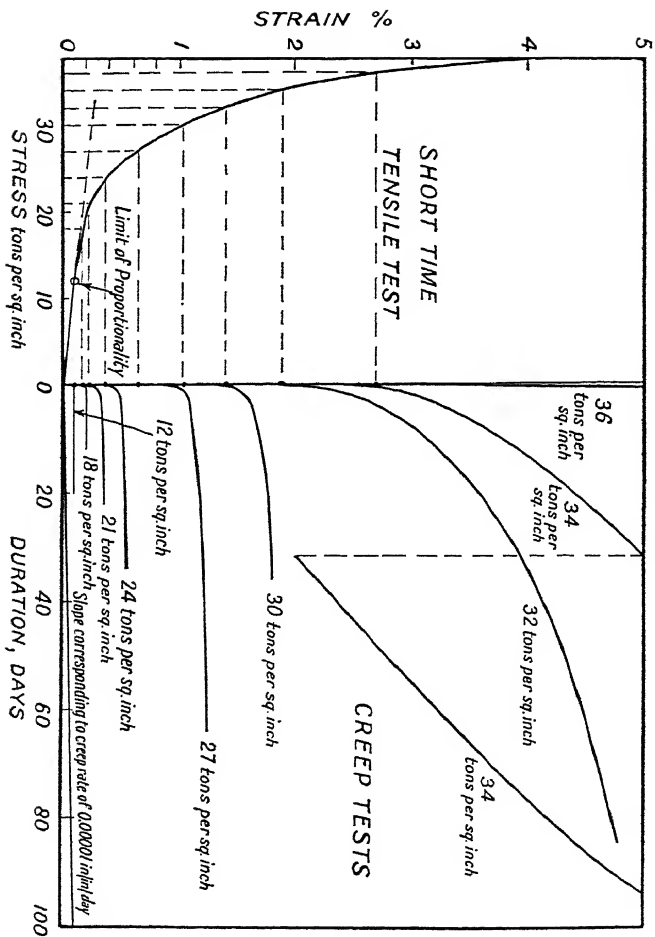


FIG. 188. Short-time and creep tests on steel at 300° C.
(Tapsell, *Creep of Metals*.)

this stress creep takes place, and after 28 days is still proceeding at a rate greater than 0.00001 inch per inch per day. In this figure it will be noted that stresses which produce very small initial deformations produce rapid creep and lead to failure in a comparatively short time. A stress of 10 tons per sq. inch which gives an initial strain of 0.1 per cent. leads to failure by creep in less than 2 days.

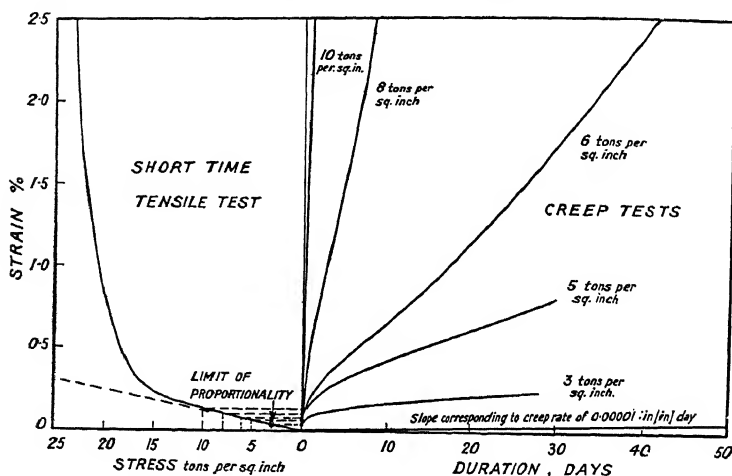


FIG. 189. Short-time and creep tests on steel at 500° C.
(Tapsell, *Creep of Metals*.)

Features of the Creep Curves.

Creep curves may be classified according to whether they show (1) creep at an increasing rate, (2) creep at a decreasing rate, followed by creep at an increasing rate to fracture, or (3) creep at a decreasing rate throughout the period of the test. The second type of curve is the general form, for in those of the first type there is usually some evidence of creep at a decreasing rate in the early stages of the test, while in those of the third type creep at a decreasing rate may give place to creep at an increasing rate if the test is continued long enough. The general type of creep curve may be divided into three portions, (1) the almost instantaneous extension that takes place on the first application of the load, and which is usually represented on the curves as extension at time zero, (2) creep at a gradually decreasing rate till a minimum rate is attained, and (3) final creep at an increasing rate. The second and third portions of the curves are separated by a point of inflexion which corresponds to the minimum rate of creep for that particular stress and temperature. It has frequently been stated that there is a period of creep at constant rate between the decreasing-rate and increasing-rate periods, but this is more accurately represented simply as a period in which the rate of change of creep rate is very slow. As the metal approaches the point at which the creep rate begins to increase, the rate

of hardening is slow, the creep rate decreases slowly, and extension takes place over the whole gauge length. When the rate of creep begins to increase, the increase is slow and is made to appear more so by the fact that the extension is now localized. These conditions tend to make it appear as if the metal was extending at a constant rate, and this appearance is exaggerated if the extension is measured with an insensitive extensometer, or if the results are plotted so that the time scale is very open compared with the strain scale, as is usually the case in curves derived from tests lasting only a day or two.

At any particular temperature the initial rate of creep is greater the greater the applied stress, and the point of inflexion at which the rate begins to increase is reached in a shorter time. As the point of inflexion corresponds to the minimum rate of creep, it may be said that the time taken to reach the minimum rate increases as the stress decreases, and that the rate of creep at the minimum decreases with the stress. In the curve representing creep under a stress of 34 tons per sq. inch (Fig. 188) the rate decreases for 35 days before the minimum rate is reached. In the curve representing creep under a stress of 32 tons per sq. inch it decreases for 85 days, and under lower stresses it continues to decrease for much longer periods.

The Limiting Creep-Stress.

Some of those who have investigated creep phenomena have reached the conclusion that creep may persist under any stress, others have concluded that once creep begins it continues and ultimately results in fracture, while others consider that there is, at least below a certain temperature, a limiting stress below which creep will not continue until fracture occurs. In practice, however, these different ideas concerning creep amount to much the same thing, for those who hold that creep may continue to fracture under any stress sufficient to initiate it admit that under certain stresses this may take an infinitely long time, and that during this time the rate of creep may be negligibly small. Tapsell considers that there is a limiting creep-stress below which creep will not continue until fracture takes place. He defines it as 'the load per unit of the original area which will just not break the bar when allowed to act on the material for a very long time'. He does not state that fracture will never occur under this limiting creep-stress, for there are no data on which to base such a claim. All that he states is that under this stress failure will not occur in what, for practical purposes, may be considered as a long time. The data relating to creep have been obtained from tests lasting a few days, weeks, and in rare cases years. These have shown that at or below the limiting creep-stress the creep rate continuously decreases and that creep eventually ceases or proceeds at so slow a rate that failure is apparently impossible within several years. The existing data do not enable any one to decide whether or not a rate of creep that has become so slow as to be incapable of measurement will ultimately

begin to increase again and so lead to fracture, but they do enable the conclusion to be drawn that under certain stresses and below certain temperatures, failure will not take place in less than say, five to ten years.

Stress-Duration Curves.

The limiting creep-stress cannot conveniently be determined by direct experiments lasting many years, and it is therefore necessary to discover some relation between the results that can be obtained in tests of limited duration and the life of a metal under particular stress-temperature conditions. At any given temperature, if stresses of sufficient magnitude are applied, failure may be produced in relatively short times. Attention has therefore been directed to the relations between the stress and the time required for fracture in order to discover whether there is not some rule that would enable the life of a metal under low stresses to be calculated, when its life under higher stresses is known. In Fig. 190 a number of stress-duration curves for different metals at different temperatures are shown, from which it will be observed that the duration increases rapidly as the stress decreases. The shape of the curves suggests either a hyperbolic form with asymptotes at some fixed value of stress, or an exponential form indicating eventual failure at all stresses, but only after a very long time at low stresses. Various attempts have been made to analyse such stress-duration curves on the assumption that they conform to some simple mathematical law, but it has not been possible to show that they can be expressed exactly by one law and by no other. Very few creep tests have been made for periods longer than 100 days, and the stress-duration curves derived from such tests seem to conform equally well either to an exponential or a hyperbolic form. Very lengthy tests would be required to show what is the correct form of the stress-duration curves, and in the meantime, extrapolation from the results obtained in tests of a few days' or weeks' duration cannot be regarded as an accurate method of estimating the stress that the metal will withstand for a period of from five to ten years.

The Minimum Rate of Creep.

At the present time estimation of the limiting creep-stress is usually based on data other than those relating to length of life under different stresses, and various methods of doing this have been proposed. Many of these are based on measurements that can be obtained from creep tests of a few hours' or days' duration, and there are marked differences in the limiting creep-stresses obtained. The most reliable method so far proposed is that due to Tapsell, based on a determination of the minimum rate of creep by means of tests lasting from thirty to forty days.

For a given metal at a given temperature the time taken to reach

the minimum rate of creep increases as the stress decreases, and the rate of creep at the minimum decreases with the stress. At a given temperature the minimum rate of creep depends only on the stress, and under a given stress it depends only on the temperature. The minimum rate of

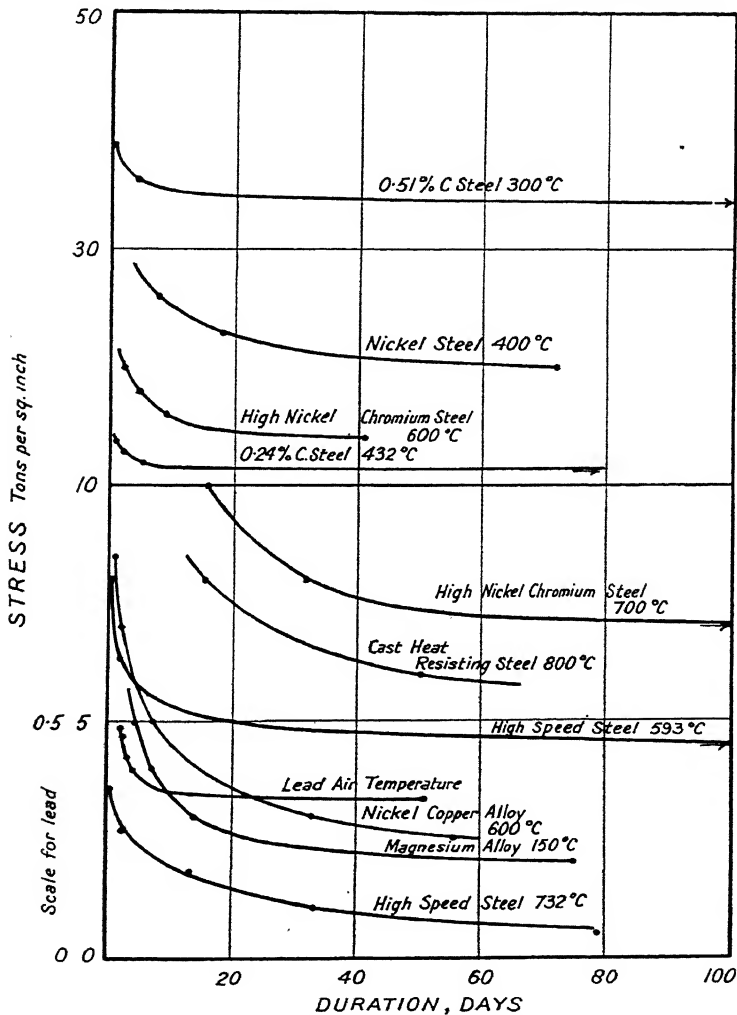


FIG. 190. Relations between stress and duration to fracture.
(Tapsell, *Creep of Metals*.)

creep may therefore be said to be a characteristic feature of the creep curve of a metal under a given stress and at a given temperature. If a certain slow rate of creep is chosen as the standard of comparison, it may be said that when the conditions are such that the minimum rate is greater than this, failure will take place in less time than when the

minimum rate is less than this. If during the period of the test the minimum rate for the stress and temperature in question is not reached, but the rate of creep at the end of the test is less than the slow rate chosen as the datum, then it may be said that the minimum rate will be less, perhaps considerably less, than the standard rate.

Tapsell, as the result of an extensive experience of creep testing, has suggested a rate of creep of 10^{-5} inch per inch per day as a suitable datum. Any stress-temperature conditions under which the minimum rate of creep is appreciably greater than this may produce failure in a comparatively short time, but any conditions that ultimately produce a slower rate of creep than this will not cause failure within a period of some years. As the rate of creep at the minimum is related to the time taken to reach the minimum, specification of a certain standard rate of creep sets a limit to the duration of the creep tests. If, e.g., under certain stress-temperature conditions, a minimum rate of creep equal to 10^{-5} inch per inch per day is just reached after 40 days, then if a higher stress or higher temperature is used the minimum rate of creep will be greater than the datum rate and will be reached in less than 40 days, whereas, if a lower stress or temperature is used the minimum rate of creep will not be reached in 40 days, but the rate of creep at the end of the test will be less than the datum rate. For carbon and low alloy steels the time required for the determination of the stress that gives a minimum rate of creep of 10^{-5} inch per inch per day is about 40 days. Under smaller stresses than this a rate of creep which is greater than the minimum but less than 10^{-5} inch per inch per day is reached in 40 days. At all temperatures below 500°C . carbon steels and steels containing small percentages of alloying elements can withstand for a long time any stress which gives a creep rate that falls below 10^{-5} inch per inch per day.

Creep Limits from Short-Time Creep Tests.

Various methods of determining the limiting creep-stress by means of short-time tests have been proposed. Such tests do not reveal the creep characteristics of metals, and it appears that they can only be applied satisfactorily as routine tests when the creep properties of the metal in question have been investigated by means of long time tests within the range of temperature concerned. It follows from a consideration of the phenomenon of creep and of the character of long-duration creep curves, that there are probably other features of these curves, besides the minimum rate of creep, that may be related to the limiting creep-stress. The creep curve for a given metal under a given stress at a given temperature is constant, and any feature of that curve, i.e. the extension on the first application of the load, the total extension during the first 24 hours, or the rate of creep at any time after the test has begun may be regarded as of equal significance to the minimum rate of creep. But it is difficult in the absence of full knowledge of the creep charac-

teristics of the metal to specify a limiting value of any of these quantities that will be associated with long life under varying conditions of stress and temperature.

There are numerous treatments such as cold working and certain heat treatments that have a marked effect on the behaviour of a metal during the early stages of a creep test, but if the metal is maintained at the temperature of the test for a sufficient time the effects of these disappear. Tests of 30 or 40 days' duration enable the metal to attain

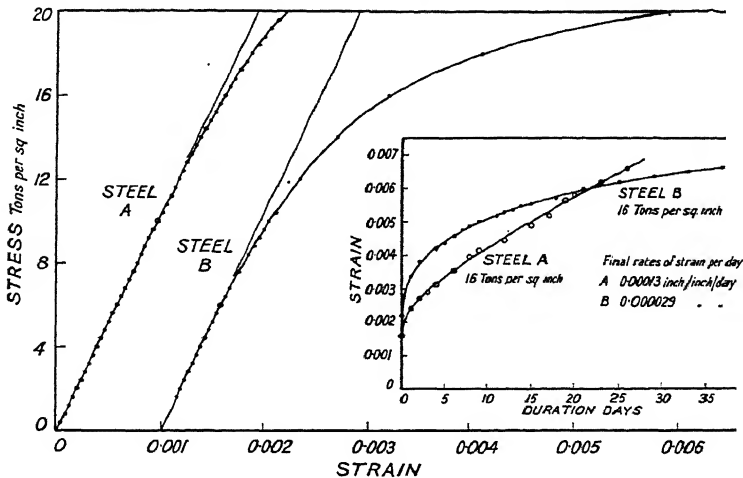


FIG. 191. Short-time and creep tests on carbon and nickel steel.
(Tapsell, *Creep of Metals*.)

to a condition of approximate equilibrium at the temperature concerned, and for this reason alone must be regarded as more reliable than short-time tests which may measure the properties of the metal in a condition that will not be maintained during a long time at the working temperature. Fig. 191 illustrates how the relative resistance to deformation at 400°C . of two different steels may vary with time. On the left of the figure are shown the stress-strain curves at 400°C . of a nickel steel *A* and a carbon steel *B*. The limit of proportionality of steel *A* is 10 tons per sq. inch, that of steel *B* is 6 tons per sq. inch. Just above the limit of proportionality steel *B* deforms rapidly with increase in stress while steel *A* deforms much more slowly. The creep curves of these steels under a stress of 16 tons per sq. inch at 400°C . are shown on the right of Fig. 191. In the early stages of the test the rate of creep of steel *B* is more rapid than that of steel *A*. But the rate of creep of *B* decreases rapidly with time while that of *A* decreases very slowly. Consequently, after a few days the creep rate of *A* is greater than that of *B*, and after 22 days the total extension of steel *A* exceeds that of steel *B* and is still extending at an appreciably greater rate. It is evident therefore that any tests lasting a few hours or a few days only

would fail to put steels *A* and *B* in their correct order from the point of view of resistance to failure under creep.

For a full discussion and comparison of the methods of estimating creep limits from short-time tests, reference should be made to Tapsell's book. It must suffice to say here that Hatfield's method (141) is based on the total deformation during the first 24 hours and the average rate of creep during the next 48 hours. Pomp and Dahmen's method (142) is based on the rate of creep between the 3rd and 6th hour, while the methods of Lea (143) and several other workers are based on the stress at which creep appears to cease after a certain short period of test. The results obtained by this last method vary considerably with the sensitivity of the extensometer and with the time that the metal is allowed to remain under stress before the creep rate is measured. Values of the creep limits of low carbon steels between 300° and 600° C. obtained by different investigators using short-time tests are compared in Fig. 192.

Total Deformation due to Creep.

Discussion of creep has so far been confined to the relations between stress and the time taken to cause fracture, but the total amount of deformation produced in a long time is also of considerable importance. Service conditions are often such that only small amounts of permanent distortion can be accommodated, and since the limiting creep-stress is frequently associated with a considerable amount of permanent distortion, attention has been directed to the study of creep from the point of view of the total deformation produced. Even at atmospheric temperature it is difficult to determine exactly the stress at which permanent deformation begins. The actual point at which it is observed to begin depends on the sensitiveness of the extension measurements, and as this is increased the elastic limit is detected at a lower stress. At atmospheric temperatures when permanent deformation takes place in amounts too small to be detected by a sensitive extensometer it can be neglected, for once started it does not continue with time. But at elevated temperatures permanent deformation may proceed for a long time although at a gradually decreasing rate, and at these temperatures the elastic limit must be defined as the stress under which no creep takes place.

At elevated as at low temperatures, permanent deformation begins gradually. There may be a certain stress below which none takes place, but at a stress greater than this by an infinitely small amount permanent deformation does begin and continues at an infinitely slow rate with time. It is therefore attempting the impossible to try to determine the stress below which no deformation occurs, for it amounts to attempting to find a discontinuity in a continuous process. All that can be determined is the stress below which no permanent set is detected within a certain time by an extensometer of a given sensitivity. If the

sensitivity of the extensometer and the duration of the test can be increased, then provided that the accuracy of the other conditions of the test is increased proportionately, the beginning of creep will be detected at a lower stress. Whether and at what temperature this

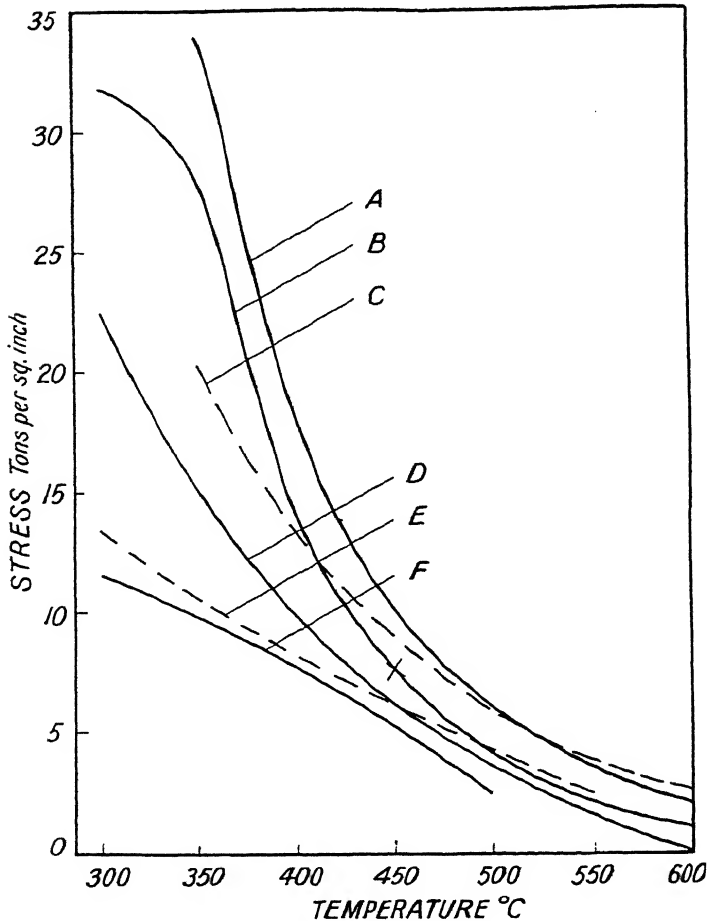


FIG. 192. Comparison of creep limits determined by short-duration creep tests. (Tapsell, *Creep of Metals*.)

creep might be detected at an infinitely small stress by an infinitely sensitive extensometer is a question that cannot be answered.

In order to be quite certain as to the amount of deformation produced by a given stress in a given time it would be necessary to keep the metal under this stress for this time and measure its extension, in which case either the actual deformation would be obtained or it would be shown to be less than the limit of sensitivity of the apparatus. In practice, however, the total deformation in a long time must be

estimated from tests of comparatively short duration. At temperatures up to about 300° C. the deformation produced on the first application of the load is large in comparison with that produced by creep, as long as the rate of creep continues to decrease. As the temperature is raised, however, the deformation due to creep becomes greater in proportion to the initial instantaneous deformation. In the early stages of creep the rate decreases rapidly, and the total creep during this period, like the initial deformation, can be actually measured in tests of comparatively short duration. After this rapidly decreasing-rate period, creep continues at a rate that is never really constant, and it is in estimating the total deformation due to this creep during periods many times longer than the period of the test that difficulty arises.

In studying the total deformation produced in a long time, investigators are concerned only with stresses equal to or less than the limiting creep-stress, for the total deformation under stresses that cause failure in less than what is for practical purposes a long time is not important. It has usually been assumed therefore that creep in this 'second period' proceeds at a constant rate, and that if the rate decreases this will cause the estimated total deformation to err on the safe side. There is a certain amount of risk, however, in assuming that the rate of creep will not sooner or later begin to increase, and therefore the total deformation calculated from tests even of 100 days' duration cannot be regarded as a safe estimate. The data that have been obtained by French, Cross, and Peterson (144), Kanter and Spring (145), and Norton (146), suffice in the meantime for purposes of design. It can neither be assumed that different batches of steel of approximately the same composition are quite similar nor that the service temperature will never exceed the nominal value. Moreover, the thermal stresses induced in a structure subjected to high and fluctuating temperatures cannot be calculated exactly, and consequently, fairly large factors of safety with respect to stress and temperature must be used. Under the circumstances therefore, reasonably accurate data regarding total deformation are all that are required, and these can be obtained, at least for temperatures up to 550° C.

The Creep Field.

In order to show the relations between the limiting creep-stress and the other mechanical properties of steel Tapsell prepared a stress-temperature chart which is shown in Fig. 193. The chart combines the results of short-time tensile tests and long-duration creep tests, and the general relations indicated refer to carbon and low-alloy steels. From the results of short-time tensile tests the curves for ultimate tensile stress, limit of proportionality, and permanent sets of 0.1, 0.2, 0.5, 1, and 2 per cent. have been plotted. From the results of creep tests the stress-temperature relations for creep rates that are either minimum rates or rates at the end of the test periods have been plotted. As already stated,

the stress under which either of those rates is equal to 10^{-5} inch per inch per day may be taken as the limiting creep-stress at the temperature concerned.

The permanent set obtained on the first application of the limiting creep-stress decreases rapidly as the temperature rises. At 300°C . the first application of the limiting creep-stress results in an extension

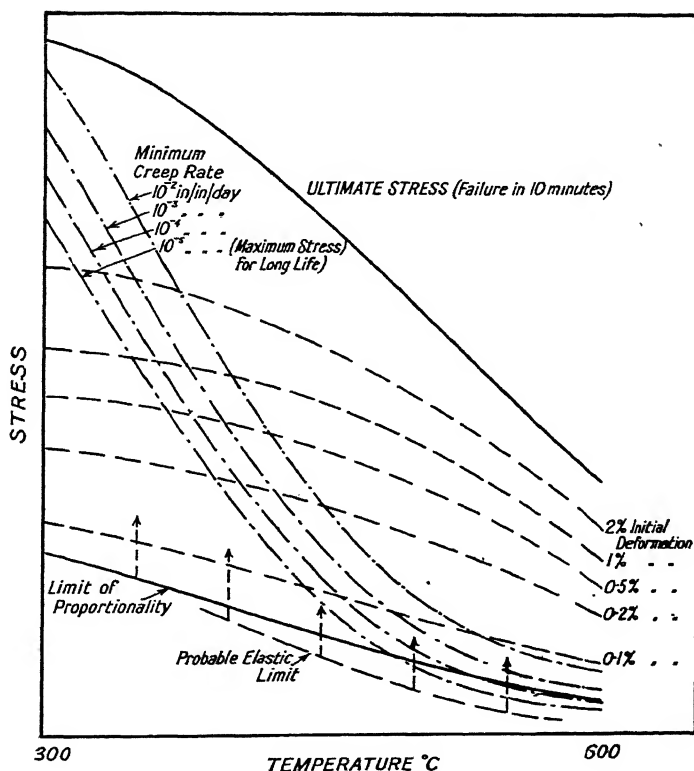


FIG. 193. The creep field.
(Tapsell, *Creep of Metals*.)

greater than 2 per cent., and for this reason, when the working temperature is near the lower limit of the creep range the limiting creep-stress (based on a minimum rate of creep of 10^{-5} inch per inch per day) is too high for design purposes. At a temperature between 450° and 500°C . the limiting creep-stress corresponds with the limit of proportionality, and the permanent set obtained on the first application is consequently very small. At temperatures above 550°C . the limiting creep-stress is below the limit of proportionality. It is evident from Fig. 193 that the limiting creep-stress is not related to the ultimate stress, the curves of constant permanent set, or the limit of proportionality.

CREEP, DUCTILITY, AND FRACTURE

The relations between time, temperature, and stress on the one hand and deformation and fracture on the other in so far as they affect the subject of this section are considered generally in Chapter IV, in the section on The Effect of Time and Temperature on the Mechanism of Deformation. In a short-time tensile test at atmospheric temperature the resistance to deformation per unit of actual area increases as the metal deforms and strain-hardens, and when the resistance to deformation becomes equal to the resistance to fracture the specimen breaks. The breaking-point is the point at which the metal has been strain-hardened to such an extent that the stress per unit of actual area required to produce further deformation is greater than that required to produce fracture. If it is supposed that the stress per unit of actual area required to produce fracture does not alter, then metals that strain-harden rapidly will reach the condition necessary for fracture after a comparatively small amount of deformation, while those that strain-harden slowly will require a large amount of deformation before reaching this condition. It follows from this that the reduction in area at the point of fracture should be small in the case of metals that strain-harden rapidly and large in the case of metals that strain-harden slowly. Still supposing that the resistance to fracture remains the same, we can further conclude that if the conditions of the test permit strain-ageing the reduction in area at the point of fracture will decrease, while if they permit recrystallization the reduction in area will increase. This conclusion follows from the fact that strain-ageing tends to increase the amount of hardening produced by a given amount of deformation while recrystallization tends to decrease it.

The above represents the normal relations between deformation, strain-hardening, strain-ageing, and recrystallization on the one hand and fracture on the other. The behaviour of different metals at atmospheric temperature can be explained in this way without supposing any difference in their breaking stress. Thus the reduction in area at the point of fracture increases in the order iron, copper, aluminium, and lead because the rate of strain-hardening decreases. The behaviour of the same metal at different temperatures can also to a considerable extent be accounted for in this way. Thus, as shown in Fig. 83 (Chapter IV), the reduction in area of iron decreases in the range in which strain-ageing takes place rapidly (200–350° C.) and then increases as the temperature is further raised as a result of a diminution in the rate of strain-hardening and an increase in the rate of recrystallization. The question now arises, to what extent do these relations remain true when varied combinations of stress, time, and temperature are considered generally?

The rate of strain-hardening means the extent to which resistance to deformation is increased by a given amount of deformation, and accord-

ing to the normal relations the amount of reduction in area that precedes fracture should increase as the rate of strain-hardening decreases. From this we may infer that when the rate of strain-hardening increases with time or temperature as a result of strain-ageing, the reduction in area at the point of fracture should decrease. This result is actually obtained and there do not appear to be any conspicuous departures from the normal relations in this respect. We may also infer that when the rate of strain-hardening decreases with time or temperature as a result of recrystallization or any other phenomenon, then the reduction in area at the point of fracture should increase. This result is frequently but not always obtained, and in many cases it is evident that as the temperature or the duration of tests is increased normal behaviour is departed from to an increasing extent.

TABLE 32

Elongation and Reduction in Area in Creep Failure after Different Periods

<i>Material</i>	<i>Temperature °C.</i>	<i>Time to fail by creep days</i>	<i>Comparative elongation %</i>	<i>Reduction in area by creep failure %</i>	<i>Reduction in area in short-time tensile test %</i>
0.5% carbon steel	400	0.5	25.0	72.5	72.5
	400	2.0	19.0	69.0	
	400	25.0	20.0	73.5	
	500	4.0	22.5	83.5	83.0
	500	24.5	31.0	83.5	
1.7% manganese steel	300	0.8	24.5	61.0	51.5
	300	2.5	22.0	60.0	
	300	25.0	25.5	69.0	
	300	110.0	24.0	56.5	
	400	6.75	16.5	28.0	
	400	42.0	14.0	23.0	24.5
	500	6.5	..	78.0	
	500	37.0	62.0	84.0	65.0
	600	2.0	..	85.0	
	600	19.0	..	81.0	88.0
	400	3.0	21.0	71.0	
	400	7.5	23.5	71.5	67.0
Stainless steel	500	2.5	..	82.5	
	500	35.5	35.0	86.5	

Providing that strain-ageing does not exercise a controlling effect on the results, the reduction in area in the short-time test should increase with the temperature of testing. This is frequently observed and examples are given in Fig. 83 and Table 22 in which the reduction in area of Swedish iron is shown to increase as the testing temperature is raised above 450°C. It is not always observed, however, and in Table 21 the reduction in area of Carbonyl iron is shown to remain constant between 15° and 950°C., while in Table 20 that of Armco iron is shown to decrease as the testing temperature is raised from 550° to 750°C. If

recrystallization is taking place while a specimen is under a constant load, it should tend to decrease the amount of strain-hardening and thus increase the reduction in area at the point of fracture. Consequently, the reduction in area in creep tests should be greater than that in short-time tests; at a given temperature it should increase as the constant load decreases, and it should increase with the testing temperature. These results are sometimes obtained, but not always, and to supplement the data given in Tables 20, 21, and 22, Table 32 compiled by Tapsell is included, while in Table 33 results taken from the four tables mentioned are arranged to show the variable effect of time and temperature on the reduction in area at the point of fracture.

TABLE 33

Results from Tables 20, 21, 22, and 32 arranged to show the Variable Effects of Time and Temperature on Reduction in Area at Point of Fracture

1. TEMPERATURE CONSTANT

(a) *Reduction in Area in Creep Test is Greater than in Short-time Test*

Temp.	Metal	Test	Reduction %
350°	Armeo iron	Short time	64
"	" "	Creep test	75
350°	Swedish iron	Short time	56
"	" "	Creep test	74
450°	Swedish iron	Short time	73
"	" "	Creep test	82
300°	1.7% Mn steel	Short time	51.5
"	" "	Creep test	60-69
500°	1.7% Mn steel	Short time	65
"	" "	Creep test	78-84
500°	Stainless steel	Short time	71
"	" "	Creep test	82-86

(b) *Reduction in Area increases with Duration of Creep Tests*

300°	1.7% Mn steel	Test of 0.8 days' duration	61
"	" "	" 25 "	69
500°	1.7% Mn steel	Test of 6.5 days' duration	78
"	" "	" 37 "	84

(c) *Reduction in Area in Creep Tests is the Same as in Short-time Test*

850°	Carbonyl iron	Short time	99
"	" "	Creep test	97
550°	Swedish iron	Short time	88
"	" "	Creep test	87
400°	0.5% C steel	Short time	72.5
"	" "	Creep test	73.5

(d) *Reduction in Area is Similar in Creep Tests of Different Duration*

550°	Swedish iron	Test of 18 hours' duration	86
"	" "	" 8 days' "	87
500°	0.5% C steel	Test of 4 days' duration	83.5
"	" "	" 24 "	83.5

(e) Reduction in Area in Creep Tests is Less than in Short-time Test

Temp.	Metal	Test	Reduction %
450°	Armco iron	Short time	81
"	" "	Creep test	33
650°	Armco iron	Short time	75
"	" "	Creep test	6
650°	Swedish iron	Short time	90
"	" "	Creep test	39
950°	Carbonyl iron	Short time	99
"	" "	Creep test	30
600°	1.7% Mn steel	Short time	88
"	" "	Creep test	81

(f) Reduction in Area decreases as Duration of Creep Test increases

600°	1.7% Mn steel	Test of 2 days' duration	85
"	" "	" 19 "	81
300°	1.7% Mn steel	Test of 25 days' duration	69
"	" "	" 110 "	56

2. THE TEMPERATURE VARIES WHILE THE DURATION OF CREEP TEST IS SIMILAR

(g) Reduction in Area increases with the Temperature

400°	0.5% C steel	Test of 25 days' duration	73.5
500°	" "	" 24.5 "	83.5
300°	1.7% Mn steel	Test of 2.5 days' duration	60
600°	" "	" 2 "	85
300°	1.7% Mn steel	Test of 25 days' duration	69
600°	" "	" 19 "	81
400°	Stainless steel	Test of 3 days' duration	71
500°	" "	" 2.5 "	82.5

(h) Reduction in Area decreases as Temperature increases

350°	Armco iron	Test of 46 hours' duration	75
850°	" "	" 46 "	20
750°	Carbonyl iron	Test of 26 hours' duration	95
950°	" "	" 19 "	30

The results collected in Table 33 show that there are pronounced variations in the effect of time and temperature. Sometimes the normal effects are produced and the reduction in area increases with the time occupied in testing and the temperature of testing, i.e. in sections *a*, *b*, and *g* in Table 33. In other cases the reduction in area remains constant or decreases when the time occupied in testing or the temperature of testing is increased, i.e. in sections *c*, *d*, *e*, *f*, and *h* in Table 33. As explained in Chapter IV normal behaviour is departed from because time and temperature may under certain conditions have a pronounced effect on the stress required to produce fracture. There is a direct relationship between stress and fracture as a result of which a metal may break under a suitable combination of stress, time, and temperature without regard to previous deformation. As the temperature at which the stress is applied or the time for which it is applied is increased, metals show an increasing tendency to fracture abnormally, and when they

do break in this way the rupture is usually wholly or partly intercrystalline. Under prolonged loading at elevated temperatures a gradual rupture of the cohesion at the grain boundaries or along the planes where slip has previously taken place tends to reduce the stress required to produce fracture. In other words, circumstances arise when fracture takes place under quite low stresses and does not therefore involve substantial previous deformation. These circumstances are favoured by increasing the temperature or the time of stressing.

It follows from the above that within certain limits time and temperature may have a similar effect to stress in producing failure, and in consequence the measurement of deformation may not be an indication of progress towards fracture. These conditions come into operation in the case of Armco iron (Table 20) at temperatures above 450°C ., in Carbonyl iron (Table 21) in a creep test at 950°C ., and in Swedish iron (Table 22) in creep tests above 650°C ., but only to a small extent. They do not appreciably affect the behaviour of steels at temperatures below 600°C ., as shown by Table 32, but they do so at higher temperatures. Tapsell describes the results of several experiments in which premature intercrystalline failure occurred. He observed it in nickel-copper alloys at 700°C ., in nickel-chromium alloys at 800°C ., in a high nickel-high chromium steel at 800°C ., and in carbon steel that failed by creep in a few weeks at 600° – 650°C . In some of these alloys most of the elongation appeared to be due to the formation and widening of cracks just as in the experiments of Hanson and Wheeler described in Chapter IV. When failure takes place in this way the deformation-time curve has quite a different form from an ordinary creep curve, and some curves for a nickel-chromium alloy studied by Tapsell are shown in Fig. 194. Under a stress of 1.8 tons per sq. inch the extension during the first 34 days was less than 0.0001 inch per inch, cracks then began to form and the specimen extended rapidly and fractured in 54.5 days. Under higher stress the cracks began to form within a shorter time, and in the early stages of the tests, before the cracks began to open out, some deformation of the crystals occurred.

COMPOSITION, TREATMENT, AND CREEP

In determining the temperatures at which alloys may be used, the melting-point of the basis metal exerts a dominant influence, for at temperatures near their melting-point the strength of metals is low, and even at those considerably below this it is not sufficient to be of practical value. The low melting-point metals lead, tin, and zinc, and alloys based on them are not suitable for use at temperatures substantially above that of the atmosphere. Copper and its alloys and certain alloys of aluminium are suitable for certain uses at temperatures up to about 350°C ., but the metals principally used under conditions that involve elevated temperatures are alloys based on iron and nickel. These alloys are considered in Parts V and VI. Between them these two metals give

rise to series of alloys that almost overlap. Plain carbon steels and nickel-copper alloys are suitable for use up to about $450^{\circ}\text{C}.$, but at higher temperatures other alloys are required. Increased resistance to creep is obtained in steel by the addition of molybdenum, chromium, and nickel, and certain other elements, and there are great variations in the combinations and amounts in which these elements are added. The creep resistance of nickel is increased by adding chromium or chromium

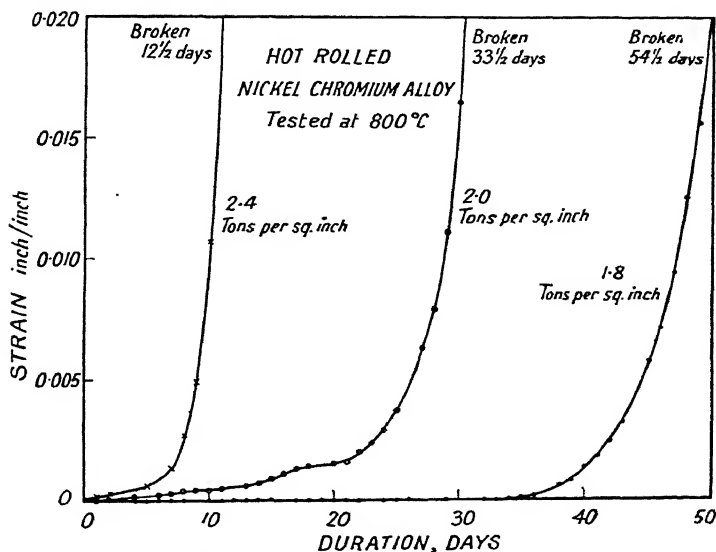


FIG. 194. Strain-duration curves for nickel-chromium alloy at $800^{\circ}\text{C}.$
(Tapsell, *Creep of Metals*.)

and iron and there is not a great deal of difference between certain heat-resisting nickel-chromium steels and nickel-chromium-iron alloys.

Increased resistance to creep means increased resistance to deformation at elevated temperatures, and it may be estimated from increased ultimate tensile strength in short-time tests or slower rates of extension in creep tests. But there is no evident reason why elements that increase the resistance of iron and nickel to deformation should also increase their resistance to abnormal fracture under suitable conditions of stress, time, and temperature. Furthermore, as these creep-resisting alloys are likely to be used at higher temperatures and subjected to greater stresses for longer times, they will be more liable to failure by intercrystalline rupture if the resistance to this is not increased. In general, alloying additions do not increase the resistance to intercrystalline failure to the same extent as the resistance to deformation, and in consequence the tendency of heat-resisting alloys to fail in this way under conditions that they might be expected to withstand from a consideration of their behaviour in tests of comparatively short duration is a problem of great practical importance.

Many of the treatments performed on metals to increase their strength at atmospheric temperature do not increase their strength at elevated temperatures. At atmospheric temperatures forged metals have better mechanical properties than cast metals, but at elevated temperatures the position is reversed. Similarly, at atmospheric temperature the strength increases as the grain size decreases, whereas at elevated temperatures the contrary is true. Increases in strength obtained by cold-working are eliminated by heating so that this treatment is of little use in improving strength at elevated temperatures. In the same way increases in strength obtained by heat treatment are eliminated by heating, and there is no object in hardening a steel for use at elevated temperature if at the service temperature it will soften progressively as a result of tempering. Metals for use at elevated temperatures should be stable at those temperatures, and if they undergo any change it should be of such a nature as to increase their resistance to deformation. The only type of change that leads to an increase in strength with time is precipitation-hardening, and a considerable amount of attention is being given to the development of alloys that will harden at the service temperature and not reach the softening stage within the period of their useful life. In general, components for use at elevated temperature are employed in the cast, forged, normalized, or annealed condition; in certain circumstances steels that do not temper at the service temperature are used in the hardened condition; while in others precipitation-hardening alloys that do not reach the softening stage at the service temperature are used.

FATIGUE AND CORROSION FATIGUE

Introduction.

In previous chapters attention has been confined to the behaviour of metals under a single application of a stress which may be gradually increased as in the tensile test, maintained for a long time as in creep tests, or suddenly applied as in notched-bar tests. It is now necessary to consider their behaviour under repeatedly applied stress. Interest in this dates from the last decade of the first half of the nineteenth century when the extensive use of iron in place of brick and masonry for bridges and other structures took place contemporaneously with rapid railroad developments. Between then and the end of the century a number of investigations on the subject were undertaken, and as a result of the pioneer work of Fairbairn (1860-1), Wöhler (1870), Bauschinger (1881), and Baker (1886), some of the most important characteristics of the phenomenon were established. The rapid engineering development in the present century, particularly in high speed reciprocating engines, turbines, automobiles, and aircraft, has been accompanied by an increased interest in the effect of repeated stress, and the recognition of its importance has given rise to numerous investigations in Britain, America, and Germany.

In some cases the repeated stress is an impact stress, but usually it is cyclic, i.e. varying gradually from, say, a given value in tension to the same value in compression. Thus repeated stressing means the repeated application of a range of stress, and much of the interest in the subject has arisen from the fact that metals may be fractured by the repeated application of a stress range of which the upper limit is considerably below the ultimate tensile stress. We have seen that the ultimate tensile strength is a characteristic feature of the short-time tensile test, and owes its significance to the fact that it is a measure of the extent to which a metal strain-hardens at such a rate that the increased resistance to deformation per unit of area more than counterbalances the reduction in area. The ultimate tensile strength is not, however, a measure of all that is implied by strength, and at temperatures below 250°C . steels can withstand slowly applied loads considerably greater than the ultimate tensile strength, while at temperatures above 400°C . they may fracture under slowly applied loads considerably less than the ultimate tensile strength at the temperature in question. Owing to the limited significance of the ultimate tensile strength it is not surprising that metals fail under the repeated application of lesser stresses, for the conditions realized in a repeated stress test are clearly different from those in a short-time test.

In the short-time tensile test a metal fractures when it has been deformed to such an extent that the resistance to deformation per unit of actual area is less than the resistance to fracture under the conditions of the test. In creep tests similar relations between deformation and fracture are frequently realized, but under suitable conditions of stress, time, and temperature, fracture may take place under much lower stresses than would be expected, i.e. after considerably less deformation of the test-piece. The characteristic feature of repeated stressing is that a metal may be brought to a condition favourable for the initiation of fracture without being deformed to the extent that would be expected from a consideration of its behaviour in a short-time test, and it may also be fractured by the repeated application of a stress considerably less than the short-time breaking stress. There are therefore two aspects of the behaviour of metals under repeated stress. One is the mechanism by means of which the metal is brought to a condition favourable for fracture, the other is the mechanism of fracture.

In the tensile test the metal is brought to a condition favourable for fracture by subjecting it to a certain amount of deformation at the point of fracture. It is not, however, the deformation that produces the required effects, but the changes that take place in the metal and lead to strain-hardening. Under repeated stressing the changes that lead to strain-hardening may proceed progressively, although the external form of the metal is not undergoing appreciable alteration, and consequently, the metal may attain the condition required for the initiation of fracture while its original shape is substantially unchanged. Strain-hardening

under repeated stressing will be described later; meanwhile, it is sufficient to state that when a metal is subjected to a range of stress varying from a given value in tension to a similar value in compression it stretches when the stress is tensile and contracts when the stress is compressive, but returns to its original dimensions every time the stress passes through zero. The external form does not change progressively as the range of stress is repeated, but the internal condition does, and more slip-bands are formed by each cycle of stress until a certain limit is reached. Thus the metal is progressively strain-hardened by the repeated application of the stress range. In the short-time test fracture occurs when the stress per unit of area on the reduced cross-section attains a certain value known as the breaking stress. Under repeated stressing fracture begins when the metal has been strain-hardened to such an extent that cracks may be initiated and propagated by the repeated application of the range of stress concerned.

Each metal has certain definite characteristics which determine its response to applied force. These are its fundamental mechanical properties. When forces of different types, e.g. tensile, compressive, or flexural, are applied at different temperatures under different conditions, e.g. gradually increasing, constant and prolonged, or repeated, a certain type of behaviour is observed and certain measurements may be made. The behaviour under one set of conditions is related to that under others through the fundamental mechanical properties, but there is no direct connexion between different sets of conditions. Thus when a progressively increasing stress is applied to a metal test-bar it breaks when the stress attains a certain intensity; when a constant stress of sufficient magnitude is applied under suitable conditions it breaks after a given time; and when a cycle of stress of suitable magnitude is repeatedly applied the metal breaks after a certain number of applications. In each case the result obtained has a bearing on the fundamental mechanical properties which control the relations between stress, time, temperature, and number of applications on the one hand, and deformation and fracture on the other, but none of the results are more fundamental or normal than the others. Thus, when we say that a metal fails under the prolonged application of a load less than its ultimate tensile stress, or under the repeated application of a stress range the upper limit of which is below the ultimate tensile stress, we do not mean that there is anything unusual in this behaviour, but simply that time and number of applications must be taken into account as well as stress.

One notable difference between repeated stressing on the one hand and short-time and creep tests on the other is that in the former there is no necking at the point of fracture. Now brittle materials break without necking in the tensile test, and when the conditions are favourable to intercrystalline fracture or other abnormal failure metals break without necking in creep tests. It might thus be deduced that there is something abnormal about fracture under repeated stress. This is not the case.

Necks are formed in bars subjected to static tension and creep because the slope of the true stress-resistance to deformation curve *A* (Fig. 29) falls below a certain value before the metal has been strain-hardened to the necessary degree. In certain ductile materials, however, in which the rate of strain-hardening does not fall off as deformation proceeds the point of fracture may be reached without necking. This occurs in some austenitic steels in which deformation leads to the formation of martensite on the slip-planes and therefore to rapid strain-hardening. Such steels may give an elongation on 2 in. of 70 per cent. and a reduction in area at the point of fracture of 60 per cent., yet they fracture without necking. So under repeated stresses metals may be strain-hardened to the degree required for the initiation of fracture without beginning to neck, for under these conditions the curve *A* (Fig. 29) does not apply and the strain-hardening effect is produced without progressive deformation. Another characteristic of failure under repeated stressing is that the fracture is different from that produced in other ways. It originates as a crack at the surface, and when the strength of the piece has been sufficiently reduced by the spread of this crack sudden fracture follows. The fractured ends of specimens broken in this way are almost plane or conchoidal and show two distinct portions: (1) a smooth area which represents the portion of the fracture produced by the gradual spread of the crack, and (2) a crystalline or fibrous area which represents the portion of the fracture that occurred suddenly.

The failure of metals under repeated stress is known as 'fatigue' and their resistance to failure of this kind as 'endurance'. In one respect the term fatigue is appropriate in that it implies that under repeated stressing the capacity of the metal to withstand the stress gradually diminishes, so that if the range is of sufficient magnitude and is applied a sufficient number of times the metal will break. In other respects, however, it is not so suitable, for in many respects the behaviour of metals under repeated stress is quite different from what is ordinarily implied by the term. If fatigue was a correct description of the phenomenon under consideration, it would be expected that the smallest range of stress would eventually break the metal if applied a sufficient number of times; whereas in the case of steel and many other metals the applied range must exceed a certain limit or failure will not take place at all. Furthermore, it would be expected that the repeated application of a range of stress by exhausting the capacity of the metal to withstand stress would lower its ultimate tensile stress, whereas it actually raises the ultimate tensile stress unless the repeated stressing has been continued until cracks have begun to form. Again, if fatigue was a correct description, periods of rest would be expected to eliminate the effects of previous stressing, and decreasing the interval between applications would be expected to decrease the number required to produce failure. Actually, however, periods of rest and frequency of application have little effect except when the frequency becomes very high; then the

number of applications required to produce failure increases as the interval between application decreases. Finally, if fatigue was a correct description, the subjection of a metal to the repeated application of a smaller range of stress would not increase its resistance to a greater range. Yet in practice this is what occurs, and when a metal is subjected to many applications of a range that is insufficient to break it, this treatment (which is known as under-stressing) increases its resistance to ranges of stress otherwise sufficient to break it. The greatest range of stress that a metal can withstand for an indefinite number of applications is known as its endurance range, and it has been shown that by the repeated application of a range less than this the endurance range may be raised by an amount that varies with the metal and the condition of stressing from 10 to 40 per cent. Thus, although fatigue is in one sense an appropriate term for denoting the phenomenon under consideration, it must be borne in mind that no conclusions as to the behaviour of metals when repeatedly stressed can be reached by considering what is ordinarily meant by the word.

Fatigue Testing Machines.

When a metal component fails in service as a consequence of fatigue, all that can usually be said is that either the material was defective or the component was badly designed, or the stresses were actually greater than was expected. Accurate information about the number of applications of different cycles of stress that different metals will withstand, or fail to withstand, has been obtained from tests made in suitable machines under controlled conditions. Numerous machines have been devised for this purpose and many investigations have been carried out on the resistance of metals to repeated bending, tension, torsion, and impact. Most of these are described in Dr. Gough's book on *Fatigue of Metals* (147) and only a brief description of the main types need be included here.

The first fatigue machine was that invented by Wöhler in 1870 and about 90 per cent. of all the fatigue tests recorded have been performed in machines of this type. In the Wöhler machine the specimen is a cylindrical cantilever, one end of which is fixed in a chuck which runs in ball-bearings. At its free end the cantilever carries a load applied through a ball-bearing. As the specimen rotates, the stress at any point on its circumference varies from a maximum in tension, when the point is on the top, to a maximum in compression, when the point is at the bottom of the specimen. The change in stress is gradual and follows a sine curve. The machine includes a counter which records the number of revolutions, and these correspond to the number of complete stress-cycles, i.e. from the maximum in tension, through the maximum in compression, and back to the maximum in tension. A complete stress-cycle is usually called a reversal, but the word has a special meaning in this connexion for it actually denotes two stress-reversals. The Wöhler test

is called a rotating-cantilever test. A somewhat similar machine invented by Sondericker and Farmer employs a beam specimen, supported at both ends in ball-bearings and loaded through ball-bearings at two points. This is a rotating-beam test.

A number of machines have been devised for applying repetitions of direct stress. In the Stanton and Bairstow machine one end of the specimen is attached to a crank, the other to a movable mass. As the crank revolves, motion is imparted to the specimen and through it to the mass. The force required to accelerate and retard this mass induces stress in the specimen, and knowing the weight and the rate of acceleration the stress can be calculated. The stress variation is approximately sinusoidal and changes in each cycle from a maximum in tension to a maximum of equal magnitude in compression. The most widely used direct stress machine is that devised by Haigh. In this the stress is applied by means of an electro-magnet, and as normally arranged the applied stress varies from a given magnitude in tension to an equal stress in compression. An initial tension or compression may, however, be applied, and the machine may therefore be made to give cycles of stress varying between different values in tension and compression, between zero and a maximum in tension or compression, or between two different values in tension or compression.

Repetitions of torsional stress are applied in the Stromeier machine, which in principle resembles the Stanton and Bairstow direct-stress machine. In the Stromeier machine the crank oscillates a rocker, which rotates the specimen first through a given angle in one direction and then through the same angle in the other direction. The motion of the rocker is transmitted through the specimen to an oscillating mass, and a twisting moment is thereby applied to the specimen. Repetitions of impact are applied in the Stanton machine, in which a round bar with a V groove is supported on knife edges and subjected to repeated blows from a falling hammer, which strikes the rotating bar at the notch twice in each revolution.

Cycles of Stress.

In all fatigue-testing machines, except the repeated blow impact machine, the applied stress varies cyclically without shock between two extreme values which are known as the maximum and minimum or superior and inferior stresses of the cycle. In expressing a cycle of stress, tension stresses are represented as positive and compressive stresses as negative. The algebraic difference between these is called the range of stress and the mid-point of the range is known as the mean or average stress of the cycle. It is customary to express a cycle of stress in the form $M \pm R/2$, where M is the mean stress and R is the range of stress. In this way all the particulars of the cycle are conveniently represented.

In general, the mean stress and the range of stress may have any value, and for convenience stress cycles are classified into three types:

(1) Alternating, when the maximum and minimum stresses are of opposite signs, (2) Repeated, when the minimum stress is zero, and (3) Fluctuating or Pulsating, when the maximum and minimum stresses are of the same sign. The special case of alternating stress in which the mean stress is zero is called 'Reversed' stress. This is the type of cycle most frequently employed, and the endurance properties of different metals are usually compared in terms of the range R or the semi-range $R/2$ of reversed stress.

If metals are subjected to different ranges of stress while the mean stress remains constant, the number of applications of stress required to produce failure increases as the range decreases, and for a given material each particular range of stress is associated with a particular 'life' or 'endurance', which is measured by the number of applications required to produce failure. The endurance of a metal under a particular range of stress may be determined directly in a fatigue machine, but the single result thus obtained cannot be said to express the endurance properties of the material. For this purpose it is necessary to know how the endurance varies with changes in the range, and many tests must therefore be made with different ranges of stress.

When a suitable series of tests have been carried out, the ranges of stress may be plotted against the numbers of repetitions required to produce fracture, giving what is known as an S/N (Stress-Number) curve for the particular mean stress used—generally zero. Such a curve represents the endurance of the metal within the limits of the stress ranges employed, but from a practical point of view the curve is of limited utility unless it is possible to read or deduce from it the magnitude of the stress range that can safely be applied to the metal in service. To obtain this it is necessary to ascertain the approximate number of times that the metal will be stressed in service, and then to determine directly the range of stress that can be applied this number of times, or else deduce this from tests made with fewer reversals.

When Fairbairn performed his classical experiments on a wrought-iron bridge girder, he considered that an endurance of twelve million loadings corresponded with the probable life of the structure, and it was therefore unnecessary to discover the stress that could safely be withstood for a greater number of applications. Nowadays, many machine and structural components are expected to have a much longer endurance than this, and Table 34, compiled by Gough (147), gives an idea of the number of repetitions of stress to which various details are subjected in the course of an ordinary 'lifetime'.

Although modern fatigue-testing machines run at a speed of from 2,000 to 4,000 reversals per minute, and therefore apply from three to six million repetitions of stress per day, it is nevertheless impracticable to carry out extensive series of fatigue experiments involving thousands of millions of reversals. It therefore becomes a matter of paramount importance to discover to what extent the results obtained in tests of

shorter duration can be extrapolated to give the range of stress that may be withstood for a very large number of applications. Table 35 contains the results of a typical endurance test performed by Stanton and Pannell on mild steel, the corresponding S/N curve of which is shown in Fig. 195. The results lie approximately uniformly along a smooth curve which tends to become parallel to the N axis when the number of reversals to fracture is large. The shape of this curve is of great importance, because if it actually becomes horizontal and remains so it indicates that below a certain limiting value of the range of stress fracture will not take place under any finite number of reversals.

TABLE 34

Approximate Service required of Various Structural and Machine Details subjected to Repeated Stresses

<i>Part of structure or machine</i>	<i>Approximate number of repetitions of stress in the 'lifetime' of the structure or machine (millions)</i>
Railway bridge, chord members	2
Elevated-railway structure, floor beams	40
Railway rail, locomotive-wheel loads	0.5
Railway rail, car-wheel loads	15
Aeroplane-engine crankshafts	18
Car axles	50
Automobile-engine crankshafts	120
Line-shafting in shops	360
Railway-locomotive axles	400
Steam-engine piston rods, connecting-rods, and crankshafts	1,000
Steam-turbine shafts	15,000

TABLE 35

Results of Typical Endurance Tests (Stanton and Pannell)

<i>Limits of stress cycle (tons/in.²)</i>	<i>Range of stress (tons/in.²)</i>	<i>Reversals to fracture (millions)</i>
±16.3	32.6	0.050
±15.0	30.0	0.164
±14.0	28.0	0.481
±13.7	27.4	0.878
±13.4	26.8	1.394
±13.4	26.8	1.264
±13.1	26.2	1.684
±12.8	25.6	2.630
±12.8	25.6	4.537
±12.7	25.4	10.000 (unbroken)

Until about 1910 it was generally held that the S/N curve did not become horizontal, and that it continued to slope towards the N axis, in which case metals would be expected to fail at any stress if the number of reversals was sufficiently large. As it is difficult to decide

from an ordinary plot of an S/N curve whether it tends to become perfectly horizontal or not, various investigators applied the method of plotting $\log S$ against $\log N$. It was then found that all the points for tests involving up to a few million reversals lay on a straight line which when produced cut the $\log N$ axis between 10^7 and 10^8 reversals. This suggested that S and N were connected by an exponential equation, and that failure would ultimately take place even with the smallest range of stress. In 1910, however, Basquin (148) made a careful

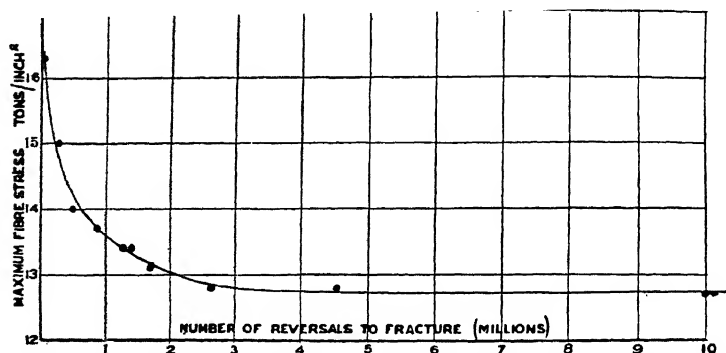


FIG. 195. Endurance tests (mild steel). Reversed bending stresses. (Stanton and Pannell. Reproduced from Gough, *Fatigue of Metals*.)

examination of the then existing data and showed that the results of tests involving more than ten million reversals tended to lie on a line parallel to the $\log N$ axis, and not on the same straight line as the tests involving smaller numbers of reversals. In other words, he showed that there was a discontinuity in the stress-number relations. Up to a point somewhere between one and ten million reversals S and N were shown to be related by an exponential equation, but for higher numbers of reversals this law did not hold, and it was therefore indicated that, below a certain limiting stress, the metal would withstand an infinite number of reversals.

Basquin's work was followed by a large number of very lengthy endurance tests which were made on a wide variety of materials by a number of investigators. Most of these tests extended to over 10^8 and a few extended to 4×10^8 , 6×10^8 , and even 10^9 reversals. As a result, it has now been sufficiently established that for many of the metals in common use the S/N curve does become horizontal. Consequently, as far as steel and many non-ferrous metals are concerned it follows that a definite minimum range of stress must be applied in order to produce failure. When the applied range of stress is lower than this the metal will safely withstand it for an indefinitely large number of reversals. The greatest range of stress that can safely be withstood for an indefinite number of reversals is known as (1) the fatigue range, (2) the limiting range of stress, or (3) the endurance range. It is on the basis

of their endurance range for reversed stresses (i.e. mean stress zero) that the fatigue-resisting properties of metals are evaluated and compared, but it is usual to express this in terms of the semi-range $R/2$ which is known as the fatigue limit, endurance limit, or limiting stress.

An endurance limit of ± 18 tons per sq. inch means that the metal will withstand indefinitely the repeated application of a cycle of stress varying between 18 tons per sq. inch in tension and the same value in compression. If, however, the duration of the tests has been insufficient to show that the applied range of stress lies on the horizontal portion of the curve, the number of reversals must be stated. Thus, if the endurance limit is given as ± 18 tons on a basis of 10^7 reversals it means that it is uncertain that the S/N curve is horizontal at this point, and that a lower stress than ± 18 tons might ultimately bring about failure.

Tests to determine Endurance Limits.

The endurance range of a material is an extremely important property, for it represents the maximum range of stress that the material will withstand for an indefinite number of applications. A large amount of information has been accumulated on the endurance of steel and non-ferrous metals in air at ordinary temperature, but much still remains to be investigated, particularly with regard to the effect of temperature and the influence of gases and liquids which have a slight chemical action on the metal under test. Meanwhile, the determination of the endurance properties under normal conditions continues, both from a research and routine standpoint. In all endurance testing the value of N at which the S/N curve becomes definitely horizontal is very important, for it determines the duration of test required to disclose the fatigue limit. This value depends on the metal, on the type of stress applied, i.e. whether direct, bending, or torsion, and on the type of specimen, i.e. whether hollow or solid.

Gough (149) tabulated a large number of data relating to lengthy Wöhler tests on different metals. From this table it is evident that in endurance tests of steel the S/N curve becomes practically horizontal at less than 10^7 reversals, so that tests of this duration will determine the fatigue limit with sufficient accuracy. Non-ferrous metals have not been so thoroughly investigated, but from the data available it appears that with these more lengthy tests are required to discover the fatigue limit. For certain of these metals tests on a basis of 5×10^7 reversals are sufficient to disclose the fatigue limit, but for others S/N curves extending to 2×10^8 and even 4×10^8 reversals show no tendency to become horizontal. More lengthy endurance tests will have to be performed on these latter materials before it can be decided whether they have a true fatigue limit or not.

When direct stress tests are made in a Haigh machine the fatigue limit is disclosed at a smaller number of reversals than in bending or

torsion tests, and in these latter the S/N curve for hollow specimens shows the fatigue limit at a smaller number of reversals than the corresponding curve for solid specimens. In bending tests the fatigue limit obtained is practically the same for hollow and solid specimens, but there is a slight tendency for the latter to give a lower value. In reversed torsion tests the fatigue limit for hollow specimens is only from 80 to 90 per cent. of that for solid specimens.

The endurance limit determined under reversed bending stresses generally exceeds that found for reversed direct-stresses by an amount that depends on the hardness of the metal. The average difference is about 8 per cent. but it is greater for soft and less for hard metals. The endurance limit under reversed torsion varies between 0.48 and 0.65 of that for reversed bending. In all types of test the number of repetitions required to disclose the endurance limit decreases as the mean stress is increased from zero.

Relation of Endurance Limit to Ultimate Tensile Strength.

No accurate and generally applicable relationship has yet been established between the fatigue limit and other mechanical properties, but the available data go to show that it is more closely related to the ultimate tensile strength than to any other property. From a survey of the data obtained from bending tests Gough has concluded that for steel the ratio of fatigue limit to ultimate tensile stress is usually between 0.4 and 0.55, and that this ratio is not greatly affected by the composition or treatment of the material. Moore and Jasper (150) consider that this ratio is approximately 0.5, while Stribeck has suggested calculation of the approximate fatigue limit from the formula: fatigue limit = $0.285(f_t - f_y)$, where f_t is the ultimate tensile strength and f_y the yield-point stress.

The establishment of an approximate relationship between the fatigue limit and a comparatively easily determined quantity like the ultimate tensile stress is a matter of considerable importance, for it enables the endurance properties of a steel to be roughly estimated without fatigue tests, and even when the endurance limit has to be determined accurately knowledge of its approximate value greatly facilitates the testing. In order to obtain an idea of the probable value of the endurance limit of steel it is not even necessary to perform a tensile test, for the ratio between the ultimate tensile strength and the Brinell hardness number is usually approximately 0.22. The endurance limit in tons per sq. inch may therefore be approximately determined by measuring the Brinell hardness and multiplying by about 0.11. With this knowledge it is generally possible to make an experimental determination of the fatigue limit with about four specimens.

The ratios given above apply to forged steel subjected to reversed bending stresses, but they do not hold for cast steel, cast iron, or non-

ferrous metals, and they must be corrected if applied to direct-stress endurance tests. It should also be stated that the ratios do not apply to all kinds of steel in all conditions, but only to sound and reasonably clean steel which is not heavily cold-worked. When the steel contains many inclusions the ratio of fatigue limit to maximum tensile stress is lowered, and the same applies to steel that has been extensively cold-worked as in wire drawing. In general, the fatigue-limit ratio tends to decrease as the hardness of the steel increases and to increase with its ductility.

The Effect of the Frequency of the Applied Cycle of Stress.

If the behaviour of metals under repeated applications of stress was affected to a marked extent by the number of cycles applied in unit time, the study of fatigue and the practical application of endurance data would be rendered very complicated. The accumulated information relating to fatigue contains results of tests performed at frequencies between 100 and 5,000 cycles per minute, and in service the frequency of the applied cycles of stress varies between wide limits. If it was necessary to take the frequency into account in testing and design it would mean that fatigue limit-frequency curves would have to be determined for each material. Some of the earlier work on the effect of frequency suggested that the fatigue limit was lowered by an increase in the frequency of the applied stress. In 1911 Hopkinson (151) carried out some tests at a frequency of 7,000 cycles per minute, which were compared with slower tests made by Stanton on the same material. The comparison indicated that an increase in frequency did not decrease the fatigue limit. Since then the problem has been studied by a number of investigators, and it is now established that the fatigue range for reversed bending stresses is not affected by variations in frequency between 150 and 5,000 cycles per minute, while for direct stresses it remains unaltered by variations between 2,000 and 6,000.

When the frequency of the applied cycle of stress becomes very high the fatigue limit is raised. This has been shown by Krouse (52) and by Jenkin (152) who used an electro-magnetic machine capable of maintaining wires in vibration at frequencies of 120,000 per minute. Three materials were tested, viz. Armco iron, mild steel, and copper, the results of some of the tests of which are shown in Table 36. More recent experiments by Jenkin and Lehmann (153) using frequencies up to 1,200,000 per minute have shown that at such frequencies the fatigue limit may be increased by about 60 per cent., whereas it is only increased by 15 per cent. with frequencies of 120,000 per minute. It was also found that the fatigue limit did not increase indefinitely with increase in frequency but appeared to reach a maximum, beyond which, in some tests, it tended to fall.

With regard to the effect of frequency on the fatigue limit, present knowledge indicates that no appreciable speed-effect exists up to 7,000

cycles per minute when the tests are performed at air temperature. At higher frequencies the fatigue limit increases until it reaches a maximum in the neighbourhood of 1,200,000 cycles per minute. Our knowledge with regard to the effect of speed at elevated temperatures is less certain, but from the available data it appears that under these conditions the effect of speed becomes appreciable at frequencies of a few thousands per minute.

TABLE 36

Results of High-frequency Fatigue Tests (Jenkin)

<i>Mild steel</i>		<i>Armco iron</i>		<i>Copper</i>	
<i>Frequency</i>	<i>Endurance limit (tons per sq. inch)</i>	<i>Frequency</i>	<i>Endurance limit (tons per sq. inch)</i>	<i>Frequency</i>	<i>Endurance limit (tons per sq. inch)</i>
3,000	±16.3	3,000	±15.75	3,000	±4.88
30,000	±16.85	30,000	±16.65	30,000	±5.01
60,000	±17.35	60,000	±16.98	60,000	±5.33
				120,000	±5.53

The Mean Stress and Endurance Range.

Most of the data on fatigue relate to reversed stresses, and it is in terms of these that different metals are compared. In service, however, they are frequently subjected to repetitions of stress ranges of which the mean stress is not zero, and it is therefore important to know how the endurance limit varies with the mean stress. For any given material this may be ascertained by direct experiment, but this involves the determination of a number of S/N curves, and requires a great increase in the resources expended in investigating the material. It would therefore be convenient if some formula connecting mean stress and endurance limit could be established.

In many materials the endurance range decreases when the mean stress is given a negative value, in others it increases; but in all materials the endurance range decreases when the mean stress is given a positive value. For mean stresses in tension this is what would be expected, for if the limiting range of stress remained constant while the mean stress was increased from zero to various values in tension, a condition would eventually be realized in which the maximum stress of the cycle would greatly exceed the ultimate tensile stress. It is therefore obvious that the fatigue limit must decrease when the mean stress is increased from zero, but the rate of this decrease can only be discovered by experiment, and the formulae connecting fatigue limit and mean stress must in the meantime be deduced empirically from the recorded results of tests.

Various equations have been proposed to express the relations between M (mean stress) and $R/2$ for the particular case in which R is

the endurance or fatigue range and $R/2$ the endurance or fatigue limit. The best known of these are (1) Gerber's Parabolic Law, (2) Goodman's Straight Line Law, and (3) Gough's Modified Goodman's Law.

Gerber analysed the results of Wöhler and Bauschinger and concluded that the relations between the endurance range and the mean stress could be represented by the formula

$$R = R_r \left\{ 1 - \left(\frac{M}{f} \right)^2 \right\}, \quad (1)$$

where R = endurance range for mean stress M ,

R_r = endurance range for mean stress zero,

f = ultimate tensile strength.

According to this formula, as M increases from zero to the ultimate tensile stress the fatigue range diminishes parabolically to zero value.

Goodman accepted the view that the effects of repeated stress are due to dynamic action. It follows from the theory of work that (a) if a load is suddenly applied to a bar, the intensity of stress produced is twice that which would be produced by a static load of equal magnitude, and (b) if a bar is carrying a static load W and this load is suddenly reversed, the stress intensity produced is three times the static stress intensity. Goodman argued that the conditions which obtained in fatigue tests were the same as those realized in dynamic loading. Consequently, it followed from (a) that the application of a range of stress varying between zero and half the ultimate tensile stress would be equivalent to stressing the metal to its ultimate tensile stress, while from (b) it followed that if the mean stress was zero the application of a range of stress equal to two-thirds of the ultimate tensile stress would produce the same result. Goodman's view was that the application of any stress less than that which would be equivalent under dynamic conditions to the ultimate tensile stress would fail to break the metal, whereas the application of any greater stress would result in fracture. The safe range for reversed stresses was therefore assumed to be two-thirds and for repeated stresses half the ultimate tensile stress. The safe range for any mean stress was supposed to be given by the linear law

$$R = R_r \left(1 - \frac{M}{f} \right), \quad (2)$$

where $R_r = \frac{2}{3}f$ (the ultimate tensile stress).

The dynamic theory was based on a fallacy and is now discredited. There is no 'live-load' effect in fatigue-testing machines in which the variation of stress is approximately sinusoidal, and the constant value of two-thirds for the ratio of endurance range to ultimate tensile stress is not obtained. Nevertheless with some metals there is a definite linear relationship between M and R (the endurance range). Such a relation is expressed by equation (2), but R_r does not have the value assigned to it by Goodman and must be determined by experiment. When modified in this way equation (2) represents the Modified Goodman Law.

Gough (147 and 149) has examined the relations between the Gerber Parabolic Law and the Modified Goodman Law on the one hand and the results obtained with different metals and different mean stresses on the other. He concludes that there is no general quantitative relation between the fatigue range and the mean stress. Some metals conform to the Gerber parabolic relation, others to the modified Goodman linear relation, while others conform to neither. In the absence of experimental data a safe (but not accurate) range of alternating stress can usually be estimated by means of the Modified Goodman Law when the safe range for reversed stress and the ultimate tensile stress are known. But it is unwise to attempt to estimate the safe range of fluctuating stresses in this manner.

EFFECT OF CHANGES OF SECTION AND SURFACE FINISH

The specimens used in endurance tests are designed and finished so that the material under investigation will exhibit its maximum resistance to repetitions of stress. On such specimens there are no sudden changes in section and the surface is finished smooth. Unless similar precautions are observed in the design and manufacture of engineering components the endurance properties as revealed by tests will not be realized in service. Sudden changes in section such as occur at screw threads, keyways, notches, and sharp corners like the junction of the web to the shaft of a crankshaft; and surface irregularities like tool marks, file marks, and accidental scratches, all tend to reduce the fatigue-resisting properties of metals, and should therefore be avoided as far as possible.

The mathematical theory of elasticity indicates that a uniform distribution of stress will not be obtained at any cross-section where the size or shape is changing, and where this change is rapid the stress concentration effects will be large. The requirements of the theory are fully realized in elastic and isotropic materials only; in metals the effects of changes in section are greatly modified by the property of ductility, and the theoretical stress concentrations are not obtained. In ordinary static tests therefore changes of section and surface irregularities do not exercise their full effect. But when repetitions of stress are applied the stress concentrations due to these factors become very large, and in some cases approximate to the full theoretical effect.

A number of investigations have been performed on the effect of sudden changes of section on the endurance limit. Stanton and Birstow (154) studied the influence of various types of discontinuities on the endurance properties under reversed direct stresses of a series of steels of different carbon contents. Their results showed that if the endurance limits of specimens with transition curves of large radius were adopted as standards, then when small radius transition curves were used the endurance limit was reduced to about 73 per cent. of that of the standard. When Whitworth V threads were cut on the specimens

the endurance limit was reduced to about 72 per cent. of that of the standard, and when the specimens were made with square shoulders it fell to 55 per cent: the figures quoted being the average for the five steels studied. Moore and Kommers (155) also studied the effect of discontinuities, and their results confirm those of Stanton and Bairstow regarding the effect of inadequate transition curves, V notches, and square shoulders.

In general, the effects of stress concentration become much more pronounced as the hardness of the metal increases. Haigh (156) found that a small circular hole in a specimen of low carbon steel had a comparatively small effect on its endurance properties, whereas a similar hole in a specimen of cold-worked steel with little ductility had an effect approximating to the requirements of the elastic theory, and reduced the endurance limit by about 53 per cent. Gough (157) investigated the effect of standard keyways cut to scale on model shafts made of steels of different carbon content. In the case of a 0.65 per cent. carbon steel the limiting range of stress for torsional stress was reduced by 20 per cent. by the keyway, whereas in a 0.02 per cent. carbon steel it was only reduced by 12 per cent. The effect of keyways of different types has been studied by Peterson (158). Table 37 based on one prepared by Ludwik and Krystof provides a further illustration of the effect of notches and changes in section on the endurance of different metals. Tests were performed on polished, notched, and expanded specimens. The notches were 60° Vs, 0.2 mm. deep with a root radius of 0.05 mm. On the expanded specimens a length of 19 mm. had twice the diameter of the portions of the specimen on each side of it, and the fillet at the shoulders was 0.5 mm. radius.

TABLE 37

<i>Material</i>	<i>Tensile strength, tons per sq. in.</i>	<i>Fatigue strength, tons per sq. in.</i>		
		<i>Polished</i>	<i>Notched</i>	<i>Expanded</i>
Brass	21.8	8.9	8.9	7.0
Mild Steel	22.3	12.1	9.5	8.3
Mild Steel	34.3	17.2	11.4	9.5
V 2 A Stainless Steel	43.0	15.2	15.2	13.4
Ni-Cr Steel. Annealed	46.8	29.9	19.1	16.5
Medium Carbon Steel	63.5	26.7	17.2	..
Ni-Cr Steel. Hard	68.6	34.3	19.1	16.5
Ni-Cr-W Steel. Hard	103.0	43.8	20.3	19.1
Cast Iron	7.4	4.5	4.5	4.5
Cast Iron	15.8	8.9	8.9	8.9

In this table the metals are arranged in the order of their tensile strengths except in the case of the two cast irons at the bottom. It will be seen that in general the fatigue limit increases with the ultimate tensile strength and that the effect of the notch and change in section

increases with the fatigue limit. The fatigue limit of ± 43.8 tons per sq. in. shown by the polished specimen of the nickel-chromium-tungsten steel is five times the fatigue limit of the brass i.e. ± 8.9 tons per sq. in. The fatigue limit of the notched specimen of this steel (± 20.3) is, however, just over twice that of the brass (8.9). The extent to which the endurance of plain polished specimens is reduced by notches, &c., is known as notch-sensitivity, and it is evident that this increases with increase in the hardness, strength, or endurance limit of the metal. This illustrates the importance of ductility in relation to performance in service, for when the design of a component requires the presence of notches and changes in section, non-ductile materials are liable to exhibit in use endurance properties that are only a fraction of those shown in tests of smooth specimens. The endurance of the notched and expanded specimens of cast iron is the same as that of the polished specimens. This is not due to ductility, for cast iron does not display this property. It is due to the fact that the graphite flakes in cast iron act as notches which lower the endurance to such an extent that other notches are without effect. Thus, in using cast iron the low endurance may be expected to remain constant in spite of changes in section, &c., consequently this metal is more suitable for certain uses than would be expected from a comparison of the endurance of smooth specimens with those of other metals. Investigations have also been carried out on the effect of different degrees of surface finish. Thomas (159) determined the effect of scratches and grooves on the endurance limit of a 0.33 per cent. carbon steel, the shape and size of the surface markings being measured by taking gelatine casts. The results obtained were compared with the estimated theoretical stress-concentration effects, and although it was found that they were small in comparison with the calculated effects the actual reduction in fatigue limit was sufficiently serious. As a result of his work Thomas compiled the figures given in Table 38 which illustrates the effect of various commercial finishes expressed in terms of the percentage reduction in fatigue limit as compared with a finely polished surface.

In addition to the effects of changes in section as exemplified by shoulders, threads, and keyways, and the effects of prepared surfaces such as are tabulated in Table 38, the endurance of metals is greatly influenced by the surface condition resulting from heat treatment, rolling, forging, and cold-working. Attention was first directed to the importance of this by the large number of failures that occurred in the springs used in automobiles and aeroplanes during the War and the following years. In 1922 a Springs Research Committee was set up by the Department of Scientific and Industrial Research and asked to investigate the problem. This committee conducted extensive researches and reported in 1931 (160). A list of the published researches is given in this report and the general conclusion was as follows:

"The investigations carried out on our behalf have included a survey of the

intrinsic properties and especially of the fatigue properties of a wide range of British spring steels. While this survey has shown that these steels can be treated so as to give very high intrinsic properties, yet these high properties are not realized in the spring material as ordinarily manufactured and used. This surprising discrepancy is due to the fact that, owing to development of surface weaknesses as the result of heat treatment or other causes, the intrinsic properties are never fully realized either in spiral springs or plates. It appears that the influence of the weak surface layer is sufficient to nullify to a great extent the advantages which should be gained by the use of properly treated high-grade spring steels.'

TABLE 38

Effect of Various Workshop Finishes (Thomas)

<i>Type of finish</i>	<i>Estimated maximum reduction in fatigue strength (per cent.)</i>
Turned	12
Coarse file	18 to 20
Bastard file	14
Smooth emery	7½
Coarse emery (No. 3)	6
No. 1 emery	4
Finer emery (O or FF)	2 or 3
Fine carborundum	2 or 3
Fine ground finish	4
Accidental scratches (maximum found) .	16

Small surface cracks resulting from quenching, scoring resulting from cold drawing, surface decarburization and irregularities due to oxidation, all tend to lessen the endurance properties of steel. The effect of surface irregularities is specially marked in springs because high carbon and alloy steels heat treated or cold drawn to give relatively non-ductile metal are used, but the findings of the Springs Research Committee apply in a large degree to all steel.

Since the publication of the above-mentioned report, work on the effect of surface condition has continued. Hankins and Becker (161) studied the effects of small surface cracks and decarburization. The possible effect of small surface cracks was first considered, and although indications were obtained that extremely small surface-markings, possibly of the nature of cracks, may occur at the surface of a quenched and tempered specimen, such defects did not appear to be a major cause of the low fatigue resistance. The effect of surface decarburization was studied and found to be very marked. Some indication of the effect of the surface condition is given in Table 39 prepared by Hankins and Becker from the results of previous workers.

In this table the effect of removing the surface produced by working and heat treatment and of polishing after machining is shown. Most of the experiments performed by Hankins and Becker were concerned with investigating methods of atmosphere control that would prevent

or substantially decrease decarburization during heat treatment. The use of controlled atmospheres in heat treatment is discussed in Part IV. Meanwhile attention may be confined to the effect of such atmospheres on endurance properties. This effect is indicated by the results given in Table 40. Before being subjected to the treatments shown the specimens were machined and polished so that the effects indicated are due to the treatment stated.

TABLE 39

Type of stress applied	Material	Endurance limit, tons per sq. in.	
		Not machined or polished	Machined and polished
Plane bending	Carbon spring steel	± 27	± 38
Reversed stresses			
Rotating cantilever	Si-Mn spring steel	± 27	± 46
Reversed stresses			
"	Cr-V spring steel	± 32	± 42.5
Reversed torsion	Cr-V spring steel	± 15	± 28

TABLE 40

*Summary of Results of Rotating Cantilever
Fatigue Tests (Hankins and Becker)*

Treatment	Endurance limit, tons per sq. in.	
	Si-Mn steel	Cr-V steel
Completely polished	± 46	± 42
Normal furnace treatment	± 27	± 32
Heavily decarburized	± 21	± 20
Vacuum treatment (1 mm.)	± 25	± 26
Vacuum treatment (0.01 mm.)	± 35	± 34
Neutral atmosphere	± 48	± 31
CO treatment	± 47	± 34
Carbonate salt bath + graphite	± 41	± 34
Carbonate and chloride bath (short immersion)	± 35	± 39
Carbonate and chloride bath (long immersion)	± 31	± 33
Cyanide bath	± 47	± 44

It will be observed that the decarburization produced in a normal furnace treatment substantially decreases the fatigue resistance, that this is further decreased by a treatment that results in heavy decarburization, that heating under a reduced pressure of 1 mm. permits sufficient decarburization to produce a decreased endurance, and that even when the pressure is reduced to 0.01 mm. decarburization is not entirely prevented. The only specimens that displayed their full endurance properties after treatment were the silico-manganese specimens treated in the neutral atmosphere, in carbon monoxide, and in a cyanide bath, and the chrome-vanadium specimen treated in the cyanide bath. This last would have a definitely carburizing action and decarburization would thus be entirely prevented. The carbon monoxide atmosphere would have a similar effect, as would the particular neutral

atmosphere used. It is therefore difficult to account for the behaviour of the chrome-vanadium steel.

In a subsequent investigation Hankins and Becker (162) compared the fatigue resistance of unmachined heat-treated steel forgings with that of the same materials when machined and polished. A 0.2 per cent. carbon steel, a 0.4 per cent. carbon steel, a 3 per cent. nickel steel, and a nickel-chromium steel were studied. It was found that the effect of the unmachined surface was not very great in the case of the 0.2 per cent. carbon steel, but it became of great importance in steels heat treated to give high tensile strengths. Thus the nickel and nickel-chromium steels gave endurance limits of ± 14 and ± 18 tons respectively in the unmachined condition and ± 28 and ± 31 tons per sq. inch respectively when machined and polished. Further data on the effect of surface condition are given by Gill and Goodacre (110) in their reports of investigations on the endurance of steel wire. The endurance of metals is profoundly affected by surface features such as changes in section, screw threads, tool marks, decarburization, &c., because fatigue fractures begin at the surface and anything that leads to a stress concentration there is liable to facilitate failure. This has been known for a long time to those who have studied the subject, but the knowledge has not reached all those in a position to make suitable use of it, and service failures arising from inadequate fillets at changes in section, rough machining, &c., are still comparatively common. In concluding this section it may be pointed out that just as a soft surface resulting from decarburization reduces the endurance of metals, so surface hardening by carburizing or nitriding raises the endurance as described in Chapter XIII.

ENDURANCE AT ELEVATED TEMPERATURES

Most of the work on fatigue has been done at atmospheric temperature, but sufficient has been done at higher temperatures to show the general effect of temperature on behaviour under repeated stressing. The investigations that have been carried out do not provide an answer to all the questions that arise in considering the relations between temperature and fatigue resistance or in comparing the effects of temperature on the ultimate tensile stress, creep resistance, and fatigue resistance respectively. For this purpose more extensive studies are required, but they have not yet been undertaken because the evidence already available shows that at elevated temperatures it is creep and not fatigue that is important. Studies of creep and fatigue have mainly been carried out for practical reasons, and as it appears that there is a range of low temperature in which steel may fail by fatigue and not by creep, and a range of high temperature in which it may fail by creep and not by fatigue, there does not seem to be any practical necessity of studying either phenomenon in the

range of temperature in which the other is the one that matters. Such studies would, however, be of considerable theoretical interest and would aid in the investigation of the mechanism of failure by fatigue and creep.

When the endurance of steel is studied at a series of rising temperatures it is found that the range of stress that can be withstood for 10^7 reversals increases with the temperature, reaches a maximum, and then begins to decrease. Thus, if the range of stress that can be withstood

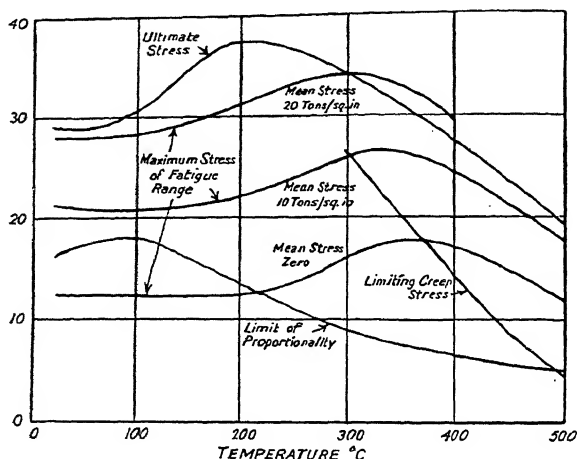


FIG. 196. Fatigue ranges of 0.17 per cent. carbon steel at different temperatures. (Tapsell, *Creep of Metals*.)

for 10^7 reversals remains a true endurance range at elevated temperature, it may be said that the curve connecting endurance range and temperature has the same form as that connecting tensile strength and temperature. The actual value of the endurance range at a given temperature depends, however, on the mean stress and so does the position of the maximum on the endurance range-temperature curve. This is shown in Fig. 196 in which the range of stress withstood for 10^7 reversals is plotted against temperature for three different mean stresses. This figure was constructed by Tapsell (163) from results obtained on a 0.17 per cent. carbon steel in a Haigh direct-stress machine running at 2,400 cycles of stress per minute. In experiments performed at the same time on the same steel the tensile strength was found to reach a maximum at about 250°C . Thus the maximum on the endurance range-temperature curve for zero mean stress occurs at a higher temperature than that on the tensile strength-temperature curve, but it moves towards lower temperatures as the mean stress is given progressively increasing tensile values. Similar results have been obtained by other investigators, but Moore and Alleman (164) obtained the maximum on the endurance range-temperature curve at

about the same temperature as that on the tensile strength-temperature curve.

In fatigue tests on steel at atmospheric temperature the controlling factors are the mean stress, the range of stress, and the number of cycles. The frequency of the cycles has little effect until it becomes very large, and the endurance range is disclosed in tests involving 10^7 cycles. The reasons for the comparative simplicity of fatigue tests at atmospheric temperature are as follows: Each cycle of stress produces a certain amount of strain-hardening in the metal, but the additional amount of strain-hardening produced by each successive cycle decreases as the number of cycles increases. Eventually a condition may be reached under which further cycles of stress produce no further strain-hardening. If this condition is reached before the metal is strain-hardened to the extent required for the formation of small cracks under the conditions realized, the applied range will be withstood indefinitely. If, however, the strain-hardening reaches the stage at which cracks begin to form before strain-hardening ceases, then the applied range will break the specimen. In general, therefore, endurance at atmospheric temperature depends on (1) the relations between repeated cycles of stress and strain-hardening, (2) the relation between repeated cycles of stress and fracture, and (3) the relations between strain-hardening and fracture. Thus it is controlled by the mean stress, the range of stress, and the number of cycles.

We have seen that when the number of cycles applied per minute becomes very large the endurance range increases. This is due to the fact that when the time of application of a stress is very short it does not produce its full effect on the metal, as shown in Chapter IV. When the number of cycles of stress per minute becomes very small another factor may come into operation, namely, strain-ageing. In endurance tests at atmospheric temperature this does not have much effect, for the tests are completed in about 3 or 4 days, and time is not allowed for substantial amounts of strain-ageing to occur. If, however, the duration of the test was considerably increased so that strain-ageing could occur, the question arises how would it affect the endurance range? We have seen in Chapter IV that strain-ageing increases the tensile strength because this depends on resistance to deformation. The endurance range also depends on resistance to deformation and strain-ageing should raise it. But failure by fatigue depends in the first instance on the metal being strain-hardened to a certain degree, and strain-ageing should decrease the number of cycles required to produce this condition. Thus, in general, strain-ageing should raise the endurance range, decrease the number of cycles required to produce failure when the endurance range is exceeded, and decrease the number of cycles required to disclose the endurance range. In short, strain-ageing should change the form of the S/N curve from that represented by *A* (Fig. 197) to that represented by *B*.

Strain-ageing does not influence ordinary endurance tests at atmospheric temperature, but it would affect them if the frequency were reduced so as greatly to prolong the tests. At elevated temperatures, however, it becomes important. Another phenomenon that may affect endurance tests is recrystallization. This does not occur in steel at atmospheric temperature, but it takes place in some non-ferrous metals at this temperature and in steel at elevated temperatures. The difference between the behaviour of steel at atmospheric and elevated temperatures, and between steel and softer metals at atmospheric

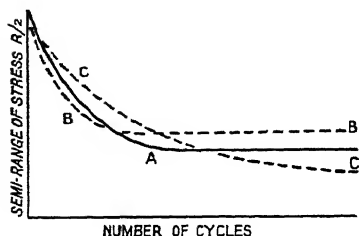


FIG. 197.

temperature, is not entirely attributable to the rate of recrystallization, for under conditions that favour recrystallization the rate of strain-hardening is small. In comparing steel with softer metals or steel at different temperatures these two factors may be taken together and it may then be said that they combine to decrease resistance to deformation and to decrease strain-hardening. Their effect is therefore in the opposite direction to that of strain-ageing, i.e. they lower the endurance range, increase the number of cycles required to produce failure when the endurance range is exceeded, and increase the number of cycles required to disclose the endurance range. In short, recrystallization and a diminution in the rate of strain-hardening should change the form of the S/N curve from that represented by *A* (Fig. 197) to that represented by *C*.

The form of the endurance range-temperature curves in Fig. 196 is due to the factors described above. As the temperature of testing is raised, the endurance range increases as a result of strain-ageing, but above a certain temperature it begins to decrease as a result of a diminution in the rate of strain-hardening and an increase in the rate of recrystallization. Up to a certain temperature the number of cycles required to disclose the endurance range would decrease and at all temperatures below this the results obtained in tests of 10^7 cycles would represent true endurance ranges. Above this temperature, however, the number of cycles required to disclose the endurance range would increase, and the results obtained in tests of 10^7 cycles would not represent true endurance ranges. Furthermore, just as a decrease in the frequency of the cycles tends to raise the endurance range when strain-ageing is taking place so a decrease in frequency tends to decrease the endurance range when recrystallization is taking place. Above a certain temperature, therefore, the number of cycles of a given range of stress that the metal can withstand will tend to decrease with the frequency of the cycles.

The number of cycles required to disclose the endurance range first

gradually decreases and then gradually increases as the temperature is raised, and at the same time the metal passes through a temperature range in which the endurance limit rises as the frequency decreases into a range in which it decreases with the frequency. As these changes are gradual it cannot be said that one set of conditions prevails below a particular temperature and another set above it, but it is, nevertheless, evident that at elevated temperatures endurance is influenced by factors that can be neglected at atmospheric temperature. In short, at elevated temperatures the number of cycles required to disclose the endurance limit increases, and it becomes doubtful whether an endurance limit actually exists. Furthermore, the number of cycles of a given stress required to produce failure decreases with the frequency of the cycles. In general, therefore, resistance to fatigue at elevated temperatures is not determined by mean stress, range of stress, and number of cycles only, but is also affected by time and thus resembles creep.

Although the available data do not permit a curve to be plotted showing the connexion between temperature and the number of cycles required to disclose the endurance limit, some examples may be given. The significance of the endurance limit at atmospheric temperature depends on the fact that it has been shown that a range of stress that can be resisted for 10^7 cycles can be resisted for an indefinite number of cycles. In tests on a steel containing 0.17 per cent. of carbon, Moore and Alleman (164) applied 4.3×10^7 cycles at 430° and 650°C. without being able to conclude that the ranges of stress resisted for this time were less than the endurance range. Lea and Budgen (165) tested a nickel steel and a carbon steel at 450°C. and found that the former broke after 3×10^7 cycles and the latter after 3.4×10^7 cycles. In general, therefore, the fatigue limit at temperatures above 400°C. is not disclosed in tests of 3×10^7 cycles, and although the exact number required is not known it is certainly more than 10^7 at all temperatures above 300°C. and increases with the temperature.

A comparison of the effect of temperature on the behaviour of metals in tensile, creep, and fatigue tests brings out a number of interesting features of the relations between the different tests. Table 41 prepared by Tapsell (163) provides data for such a comparison, and the results that have been obtained in other investigations are in general agreement with those in this table.

It will be seen in the first place that the upper limit of the endurance range for reversed stress (i.e. mean stress zero) is always considerably less than the ultimate tensile stress, but when the mean stress has a suitable value in tension the upper limit of the endurance range may exceed the ultimate tensile stress. This is shown to occur at room temperature when the mean stress is 22 tons per sq. inch, at 300°C. when the mean stress is 30 tons per sq. inch, at 400°C. when the mean stress is 24 tons per sq. inch, and at 500°C. when the mean

stress is 14 tons per sq. inch. It would also occur at 100°C. and 200°C. if tests were carried out with higher mean stress than those used. Thus whereas a conspicuous feature of reversed stresses is that the upper limit of the endurance range is considerably lower than the ultimate tensile stress a conspicuous feature of fluctuating stresses is that the upper limit of a safe range may exceed the ultimate tensile stress.

TABLE 41

Comparison of Results obtained in Tensile, Fatigue, and Creep Tests at Different Temperatures

Temp. ° C.	Endurance range tons per sq./in.	Upper limit of cycles tons per sq./in.	Tensile stress tons per sq./in.	Yield stress tons per sq./in.	Proportional limit tons per sq./in.	Limiting creep-stress tons per sq./in.
Room	0 ± 12.5 11 ± 11 22 ± 7.2	12.5 22 29.2	28.5	16.8	16	..
100	0 ± 12.3 10.5 ± 10.5 21 ± 8	12.3 21 29	30.5	18.5	18.2	..
200	0 ± 12.3 11.5 ± 11.5 23 ± 11.0	12.3 23 32	37.6	17.1	13.5	..
300	0 ± 16 15 ± 15 30 ± 8	16 30 38	34.3	..	8.6	26
400	0 ± 16.8 13 ± 13 24 ± 6	16.8 26 30	27.8	..	6.5	14.5
500	0 ± 11.7 8.5 ± 8.5 14 ± 6	11.7 17 20	19.4	..	5.0	4 to 5

The endurance ranges shown in Table 41 are based on 10^7 cycles and may be regarded as true endurance ranges up to 200°C.; at 300°C. and higher temperatures larger numbers of cycles would be required to disclose the true endurance range. For these higher temperatures the limiting creep-stress is given in the last column and it will be observed that (1) at 400° and 500°C. the upper limits of all ranges exceed the limiting creep-stress, (2) at 300°C. the upper limits of ranges of fluctuating stresses exceed the limiting creep-stress, (3) at 500°C. the mean stress for both ranges of fluctuating stress exceeds the limiting creep-stress, and (4) at 300° and 400°C. the highest mean stresses of 30 and 24 tons per sq. inch exceed the limiting creep-stress. It follows therefore that at 300°C. and higher temperatures steel can withstand without fracture many million cycles of stress of which the superior limit and even the mean stress exceeds the limiting creep-stress. This

relationship between endurance and creep has been confirmed in several other investigations of which the most recent is that of Moore and Alleman (164) who used tests of 4.3×10^7 cycles.

The relations described above are of considerable significance. Superficially, they appear to show that at elevated temperatures the resistance of steel to repeated cycles of stress is greater than its resistance to constant static stress. Actually, they show that fatigue and creep are two very different phenomena and are controlled by different factors. Creep is controlled by temperature, stress, and time, while fatigue is controlled by range of stress, mean stress, and number of cycles. Creep in steel is characteristic of elevated temperatures when under a constant load the cross-section of the specimen slowly decreases and consequently the stress increases until the breaking stress is reached. Fatigue is characteristic of room temperature when under repeated cycles of stress the metal strain-hardens until small cracks begin to form. A slow rate of strain-hardening and a high rate of recrystallization favour creep, but they have the opposite effect on fatigue for they prevent or retard the production of the strain-hardening required to initiate failure. Thus at elevated temperatures there is a tendency for the slow rate of strain-hardening and the high rate of recrystallization to prevent the realization of the conditions characteristic of fatigue and repeated cycles of stress have little effect in this direction. These same factors, however, facilitate the continuous extension of the specimen under the cycles of stress, and failure may result in this way. Consequently, in the range of creep the endurance of a metal is not controlled by mean stress, range of stress, and number of cycles, but by time and the creep-stress equivalent of the range of stress and its frequency.

At all temperatures a given range of stress repeatedly applied has a certain fatigue value which indicates its capacity to produce failure by fatigue when applied a certain number of times. In the creep range it has also a certain creep value which indicates its capacity to produce failure by creep after a certain time. In so far as the fatigue value of the range is concerned an increase in the frequency of the cycles should decrease the number required to produce failure. In so far as the creep value is concerned an increase in the frequency should decrease the time required to produce failure. The exact relations between temperature, time, range of stress, mean stress, frequency, fatigue, and creep are not known, but it may be said in general that as the temperature becomes higher and the frequency lower the creep value of a given range increases in importance relative to the fatigue value.

Fatigue and creep can be distinguished in two ways: (1) by observing the type of fracture when failure takes place, and (2) by measuring the deformation of the specimen during the test and plotting this against time and the number of reversals. In the tests performed by Tapsell at 500° C. (Table 41) the specimen subjected to the range

14 ± 6 broke after 15.32×10^6 cycles and showed a characteristic tensile fracture with a neck. During the test the machine had to be constantly adjusted to take up the extension due to creep and it is clear that in this case failure was due to the creep value of the applied range. Similarly, the specimen subjected to the range 24 ± 6 at 400°C . broke with a tensile fracture after 19.22×10^6 cycles ($5\frac{1}{2}$ days) and

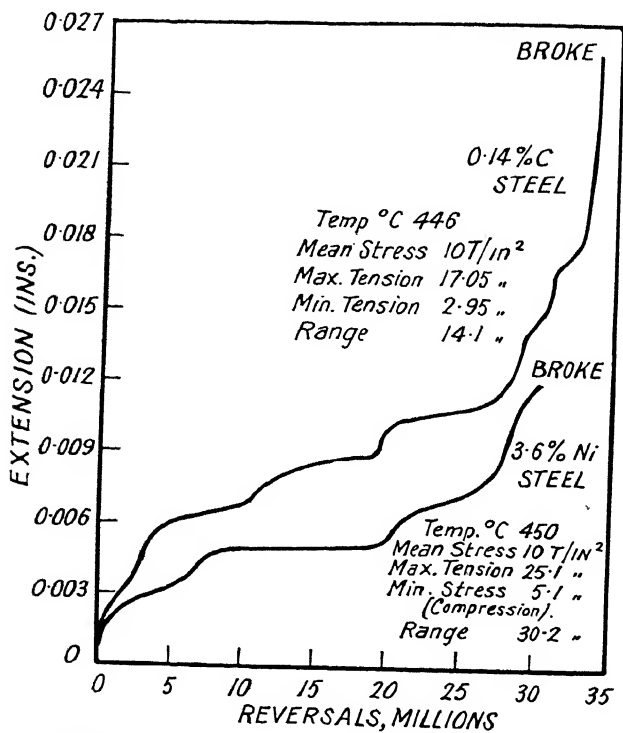


FIG. 198. Extension of steel specimens during fatigue tests at 450°C ., according to Lea and Budgen.
(Tapsell, *Creep of Metals*.)

that subjected to the range 30 ± 8 at 300°C . continued to extend during the test. Lea and Budgen (165) have published curves showing extension with time during fatigue tests at elevated temperature. These are shown in Fig. 198 and although they are somewhat irregular the general form is that of creep curves. The mild steel specimen withstood 34 million and the nickel steel 30 million cycles before fracture. These cycles were applied in about 12 days, and it is evident that failure was produced in this time by a process of creep engendered by the cycles of stress used. A static stress that could produce fracture in this time would be equivalent from the point of view of creep to the fatigue ranges applied, but many experiments would be required to discover

how the different elements in the fatigue tests, i.e. mean stress, range, and frequency contributed to the creep value.

Fatigue tests and creep tests are both endurance tests. The former determine resistance to repeated cycles of stress in terms of the number of cycles. The latter determine resistance to static stresses in terms of time and to repeated cycles in terms of time and frequency. At atmospheric temperature repeated cycles of stress produce certain changes in the metal and these result in fracture or in the attainment of a condition that is associated with indefinite resistance. Similar conditions prevail up to about 250° C., but above this the characteristic changes associated with fatigue are not so readily produced, and as the temperature rises above 300° C. the importance of these changes diminishes. At the same time, however, the characteristic changes associated with creep begin to take place to an increasing extent under repeated cycles of stress. Below 250° C. repeated cycles give rise to fatigue only. Above 300° C. they give rise to fatigue and creep. In a given case it is possible to discover by observing the fracture or measuring the extension whether fatigue or creep is the more important phenomenon. Furthermore, it is possible to say in general that above 300° C. fatigue becomes less and creep more important with rising temperature, but it is not yet possible to discover without experiment the creep-stress equivalent of a given range and frequency. In other words the effect of mean stress, range of stress, and frequency on the creep-stress equivalent at a given temperature cannot be calculated.

THE MECHANISM OF FATIGUE

The fracture of metals under the action of applied stress generally involves three distinct stages: (1) slip along crystallographic planes resulting in a change in the crystal structure and strain-hardening, (2) the initiation of a crack at some point where a considerable amount of slip has taken place, and (3) the propagation of this crack to form a fracture. There are several apparent exceptions to this average behaviour. When, for example, very hard and brittle metals are tested, the first stage is either absent or inconspicuous and fracture begins without slip and strain-hardening taking place to any appreciable extent. Again, when very plastic metals are tested there is plenty of slip but little strain-hardening, and fracture in tension seems to be produced by the simple operation of deforming the metal until the cross-section becomes negligibly small. These apparent exceptions are, however, just extreme examples of the general case, but failure by intercrystalline fracture under suitable conditions of stress, time, and temperature is a definite exception. Nevertheless, despite this instance of abnormal behaviour it may be said that the typical mechanism of failure involves strain-hardening to a certain extent, the initiation of a crack in the strain-hardened metal, and the propagation of this crack.

In the tensile test the necessary amount of strain-hardening is produced by progressively increasing the stress, and when the breaking stress is reached, the metal fractures. In tensile-creep tests the conditions are similar except that the strain-hardening and reduction in cross-sectional area are produced by the combined influence of stress and time. In fatigue tests they are again somewhat similar except that strain-hardening is produced by successive cycles of stress, that cracks are initiated by the influence of the repeated cycles on the strain-hardened metal and propagated by the effect of further cycles on the cracks. Metals will not fracture in a tensile test until the combined effects of the reduction in cross-sectional area and the increasing load lead to the stress reaching the breaking stress. They will not fracture in a creep test until continuous deformation with time has reduced the cross-sectional area to the point at which the applied load divided by the reduced area equals the breaking stress, and they will not fracture in a fatigue test unless the applied cycles of stress are of sufficient magnitude to strain-harden the metal to such an extent that cracks will begin to form under the action of these cycles. Strain-hardening is an essential feature of fatigue but it is not essential to failure in tensile or creep tests. Nearly all metals undergo some strain-hardening in short-time tensile tests, but they would eventually break on a small cross-section even if this did not occur. Similarly, metals generally undergo strain-hardening in creep tests but they would break in less time if this did not occur. In fatigue tests, however, these conditions do not arise, and if metals do not undergo a sufficient amount of strain-hardening under the repeated cycles they finally break by creep and not by fatigue as shown in the last section.

Hysteresis.

When steel is loaded to a point within its range of apparent elasticity and the load is maintained constant the metal extends slowly with time. Using sensitive methods of detecting extension a slow creeping may be observed to continue for months after the force is applied. On removal of the load the metal contracts along a line parallel to the line of extension during the original loading, and under no load it remains extended by an amount equal to the creep that took place under constant load. If allowed to remain unloaded the metal contracts with time until it returns to its original length. This slow extension and contraction with time has been called 'elastic afterwork' or 'elastic after-effect'. Furthermore, if steel is stressed to a point below its apparent elastic limit and the load is immediately removed, the unloading will not coincide with the loading line. As a result of the phenomenon of elastic after-effect the extension corresponding to a given stress is greater during unloading than during loading. If the cycle of loading and unloading is repeated a number of times the loading and unloading curves form a closed loop. This is known as

a 'hysteresis loop', and the phenomenon has been called 'elastic hysteresis'.

Various explanations of the phenomenon designated elastic after-effect and hysteresis have been proposed, for it is evident that this behaviour is not in accordance with true elasticity. The difficulty arose, however, owing to the assumption that the limit of proportionality or elastic limit determined with an extensometer of given sensitivity indicated a stress below which the deformation was truly elastic. Consequently, when the behaviour at stresses below these limits departed from what would be expected from an elastic material some specific explanation of the phenomenon appeared to be demanded. It is now recognized that the limit of proportionality or elastic limit is an arbitrary point at which departure from a linear relationship between stress and strain, or the first appearance of permanent set, is detected by an extensometer of given sensitivity in tests conducted under certain conditions with regard to time and rate of loading. When therefore a specimen is subjected to a stress below the apparent limit of proportionality and found to creep, the creep is not a peculiar aspect of elastic behaviour but is actually plastic deformation. When the specimen is unloaded, however, it slowly creeps back to its original length, and it is therefore evident that the plastic strain with which we are here concerned differs from that previously considered in not being permanent. A similar phenomenon is involved in the formation of the hysteresis loop, which is accounted for by the fact that some plastic strain takes place during loading and is recovered during unloading. This gives rise therefore to the idea of reversible plastic strain. Such a phenomenon is not consistent either with elasticity or plasticity, but it is not inconsistent with conditions under which both occur. Thus when a metal is deformed, elastic and plastic strains are produced simultaneously as described in Chapter III. On unloading, elastic recovery takes place, and it appears that the stresses involved in the elimination of elastic strain are capable of producing some plastic strain. The exact mechanism of this cannot be described. But it is known that deformation is accompanied by complicated changes in the structure of the individual crystals and in the relations between them. Some of the changes are elastic and reversible while others are plastic and permanent, and it is not difficult to suppose that when the elastic changes are reversed they have the effect of producing a certain amount of reversed plastic strain before equilibrium is restored.

If the amount of plastic strain during loading is small, the stresses associated with elastic recovery are sufficient to bring the metal back to its original dimensions by producing reversed plastic strain. For example, consider a test-bar of iron subjected to a very small stress which induces plastic strain in a few isolated crystals only. On unloading, the majority of the crystals will tend to return to their original shape, but those that were plastically deformed will tend to retain a

slightly altered shape. So long as cohesion is maintained between the crystals, however, those that were plastically deformed must return to their original shape before the elastic strain can be eliminated. Thus some further plastic deformation of these crystals must be produced by the stresses exerted on them by their neighbours. Consequently, when a metal is subjected to a cycle of stress which produces only a small amount of plastic strain on loading, the specimen as a whole and the constituent crystals return to their original shape on unloading. The condition of the metal at the conclusion of the cycle is not, however, the same as at the beginning, for although the reversed plastic deformation restores the crystals to their original shape it does not eliminate the changes associated with slip, and it actually accentuates these changes by producing more slip.

If the stress to which the specimen is subjected during the first loading produces a substantial amount of plastic strain the stresses associated with elastic recovery will not be sufficient to restore the metal to its original dimensions. A certain amount of reversed plastic strain will be produced by the elastic recovery, but the remainder of the deformation will be permanent. A hysteresis loop is therefore the result of the combination of elastic and reversible plastic strain. When the stress range covered by the loop is small so that a given ratio between plastic and elastic strain is not exceeded, the whole of the plastic strain may be reversible. When, however, the stress range is greater and the amount of plastic deformation produced during loading exceeds that which can be produced in the reverse direction by the stresses associated with elastic recovery, then some of the plastic deformation is permanent.

It was pointed out in Chapter III that the stress-strain curve with a range of apparent elasticity and a rapid permanent extension at the yield-point is typical of iron and steel only. The general stress-strain curve for metals is practically smooth, and in considering the relations between deformation and cycles of stress, attention may be confined in the first place to this type of curve. The curve *ABT* in Fig. 199 represents the stress-strain curve of a metal. If it is subjected to a cycle of reversed stress, beginning with tension, it extends along the line *ABT* until the superior limit of the cycle is reached at *B*. When the tensile stress is reduced, however, the metal does not contract again along the line *BA*. Part of the deformation produced at *B* is permanent and the metal contracts along *BC* which represents the elastic recovery and the reversed plastic strain associated with it. At *C* the stress reverses and the metal is compressed along the curve *CD* until the inferior limit of the cycle is reached at point *D*. As the compressing stress is reduced the metal extends along the curve *DA* and resumes its normal length when the zero stress point is reached at *A*.

The external dimensions of the specimen are the same after the cycle of stress as before, but the inner structure of the metal has been altered.

During the first deformation in tension slip takes place on certain planes in the crystals. During compression it does not occur in a reverse direction along the same planes, but on new planes. Thus at the end of the cycle the metal differs from its original state in that a certain amount of slip has taken place in the crystals and a certain amount of strain-hardening has been produced. In Chapter III it was pointed out that the crystal slip produced by a given load at the first application does not represent all that can be produced by that load, and therefore further slipping takes place during successive applications of the load. Thus if the cycle of stress already described is repeated, the metal neither behaves elastically within the range of stress, nor does it undergo deformation to the same extent as during the first cycle. The planes most favourably situated for slip have already been used, and the metal therefore exhibits a greater resistance to deformation. The second loop is therefore smaller than the first. With repeated cycles of stress it becomes gradually smaller, less slipping taking place each time. After a certain number of cycles it becomes of the form represented by *AEFDA* (Fig. 199). After a sufficient number of stress cycles have been performed the metal

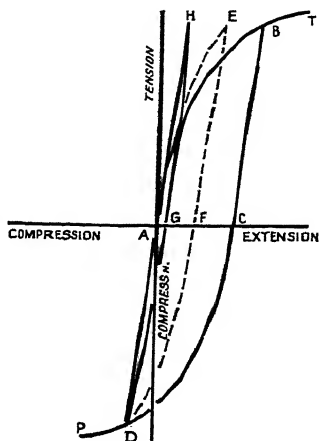


Fig. 199.

attains a cyclic state, i.e. the amount of plastic strain produced during the loading parts of the cycle is the same as the amount of reversed plastic strain produced during the unloading parts. At this stage the hysteresis loop as measured with an extensometer may appear to be a straight line, and the original theories of fatigue assumed that after a sufficient number of cycles of a range of stress less than the endurance range the metal became elastic in this range. Thus according to Bauschinger (167) and Bairstow (166) metals when subjected to cycles of stress may acquire a natural range of elasticity. If the applied range of stress is greater than the natural range of elasticity, it will eventually break the metal; if it is not, the metal will withstand it indefinitely. Recent work on 'damping capacity', which is described briefly below, has shown, however, that metals do not become elastic within the limits of the ranges of repeated stress to which they are subjected, and whether the ranges are above or below the endurance range each cycle of stress is accompanied by reversible plastic as well as elastic strain.

When therefore a metal has been subjected to a certain number of cycles of stress it attains a condition in which each cycle of stress produces a certain amount of recoverable elastic strain and a certain amount of non-recoverable plastic strain. As each increment of plastic

strain, whether it occurs during the loading or unloading parts of the cycle, is associated with certain changes in the crystal structure and strain-hardening of the metal, it is not difficult to understand why a sufficient number of stress cycles should bring the metal into a condition in which minute cracks begin to form. It is difficult, however, to account for the fact that when the range of stress is less than a certain magnitude the metal may withstand an indefinite number of cycles. According to the original view that metals could develop a natural range of elasticity under repeated cycles of stress, the difference between a safe and an unsafe range could be ascribed to the fact that under a safe range the metal became elastic and reversible before it was strain-hardened to the point at which cracks could begin to form, while under an unsafe range cracks began to form before the metal attained the elastic and reversible condition. Now that it is known, however, that metals can undergo reversible plastic deformation for an indefinite number of applications of a safe range this distinction cannot be made. Consequently, all that can be said is that if the amount of reversible plastic deformation produced during each cycle is less than a certain maximum the metal will withstand it indefinitely, whereas if it is more the metal will ultimately fracture. For convenience of reference the condition under which the plastic strain produced during each cycle is insufficient to produce eventual failure may be described as 'reversible'.

The view that elastic recovery during the unloading part of a cycle is accompanied by further plastic deformation is necessary to explain the effects of varying the inferior limit of cycles of fluctuating stress when the superior limit is maintained constant. Bairstow (166) performed a series of experiments using fluctuating tensile stress, the superior limit of the range being kept constant while the inferior limit varied. He found that as long as the inferior limit was above a certain value the range was safe, but that if the inferior limit was reduced below this the range became unsafe. It is evident that if the metal contracted elastically during unloading the extent to which it was unloaded should not affect it. Permanent deformation accompanied by slip should take place only during loading, and its extent should depend on the superior limit and be independent of the inferior limit. In order to explain the effect of fluctuating and repeated stress it is therefore necessary to suppose that some slip or other irreversible change takes place during unloading, i.e. elastic recovery of a permanently deformed metal is accompanied by a certain amount of slip on new planes or a certain change in the conditions on existing planes.

The behaviour of metals under cycles of repeated or fluctuating stress must be approximately as shown in Fig. 200. During the first stressing up to the superior stress of the cycle the metal extends along *AB*. During unloading it contracts along *BC* and the elastic contraction is accompanied by an irreversible change that increases the degree of strain-hardening at certain points. During the second loading the

metal extends along CD , more slip occurs and a further absolute extension takes place. After a few cycles, if the range is a safe one, further absolute extension will cease and the width of each successive loop will diminish, but nevertheless during each cycle some slip bands will form, and the condition of the metal will change progressively until it becomes completely reversible within the range of stress employed. If the applied range exceeds the endurance range by a small amount the same effects will be observed, but before the metal becomes completely reversible, cracks will begin to form in regions where large amounts of slip have occurred. Then the loop will begin to widen, absolute extension will recommence, and fracture will eventually occur. If the applied range exceeds the endurance range by a considerable amount, the cracks will appear while the loop is still wide and before absolute extension under each cycle of stress has ceased.

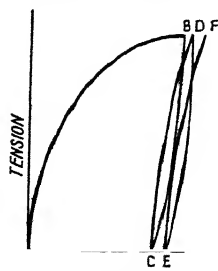


FIG. 200.

The apparent elastic limit or limit of proportionality has no significance from the point of view of fatigue. Metals such as annealed copper which have no primitive elastic limit have definite endurance ranges. In Armco iron which has a low limit of proportionality the superior stress of the safe range for reversed stresses is above this limit, while in high carbon steels the superior stress of the safe range for reversed stresses is below this limit. Under fluctuating stresses, however, both the superior and inferior limits of safe ranges may be above the limit of proportionality. Similarly, the yield-point as exhibited by iron and steel has little significance, and under repeated cycles of stress of which the superior limit is below the yield-point appreciable amounts of permanent distortion may occur.

When steel is tested at atmospheric temperature there is a critical distinction between safe and unsafe ranges as shown by the S/N curve (Fig. 195). If the range of stress is safe the metal attains a reversible condition before cracks begin to form, whereas if it is unsafe cracks begin to form before the reversible condition is attained. Once cracks begin to form they are propagated by further cycles and the metal will eventually fail. This propagation is due to the concentration of stress at the end of the cracks and the metal tends to adjust itself to the stress concentration by further permanent deformation which results in a rise in its temperature. In very ductile metals the propagation of cracks may be very slow. Thus Gough and Sopwith (168) in a specimen consisting of two crystals of aluminium observed that cracks which first became microscopically visible after 3×10^6 cycles were still propagating slowly after 29×10^6 cycles. Once the cracks have extended to the requisite extent the specimen fractures suddenly, and as the surface of the fracture produced in this way differs from that produced

by the gradual spread of the cracks the fatigue fracture generally shows two distinct regions.

In the case of steel at atmospheric temperature it is possible to state with considerable probability that a range of stress that is withstood for 10^7 cycles will be withstood indefinitely. This arises from the rate of strain-hardening of steel which ensures that with considerably less than this number of cycles the metal will have attained a cyclic state unless cracks have appeared. In steel at temperatures above 300°C . and in soft metals at atmospheric temperature the rate of strain-hardening is less and consequently a larger number of cycles of stress is required to initiate cracks, to reach a cyclic state, or to propagate cracks when formed. Thus under these conditions a larger number of cycles is required to disclose the endurance range. When the rate of strain-hardening is very small or when the effects of strain-hardening are eliminated by recrystallization the number of cycles required to initiate cracks, produce a cyclic state, or propagate cracks to fracture may be so large as to make it extremely difficult to discover whether or not a true endurance range exists.

Damping Capacity.

If a truly elastic material is subjected to a cycle of stress, then whether the cycle consists of reversed, alternating, repeated, or fluctuating stress, the stress-strain curve of the cycle will be a straight line. If, however, the material undergoes reversible plastic deformation during the cycle the stress-strain curve will be a hysteresis loop. The area enclosed by this loop represents the amount of energy expended during each complete stress cycle. If vibrations are started in an elastic material there is no tendency for them to die out unless this effect is produced by external conditions. When, however, the material undergoes reversible plastic strain some energy is converted into heat during each vibration, and therefore the amplitude of the vibrations decreases and vibration eventually ceases without any external influence being required. The capacity of a material to cause vibrations to die out is known as its damping capacity, and in the case of metals this is due to plastic strain which converts the energy of vibration into heat.

In recent years the damping capacity of metals has been the subject of a number of investigations and reference may here be made to the work of Föppl (600), Dorey (601), Bacon (602), Brophy (603), and Förster (604). The methods of measuring this property are described by Föppl and Förster and attention may here be confined to some of its implications. It has been shown that specimens subjected to cycles of stress below the fatigue limit can dissipate an unlimited quantity of energy as heat without any damage, i.e. reversible plastic strain may continue indefinitely without any sign of ultimate failure making its appearance. Thus Föppl carried out a test at 700 cycles per minute for

three years and although the metal underwent an appreciable amount of plastic deformation during each cycle and dissipated enough heat to maintain its temperature above 100°C . it was withdrawn from the test after 11×10^8 cycles and showed no sign of damage. Thus damping is no indication of ultimate failure and the capacity for undergoing reversible plastic strain does not become exhausted after a certain number of stress cycles. The damping capacity as indicated by the area enclosed by the hysteresis loop varies from metal to metal, and in a given metal it varies with the magnitude of the range of stress, the mean stress, and the number of cycles to which the metal has been subjected. In order to make comparisons between different metals Föppl has adopted the method of determining the damping capacity under cycles of stress equal to the endurance range after the metal has been subjected to a sufficient number of cycles to reach a steady state.

In addition to its bearing on the behaviour of metals under repeated cycles of stress the study of damping capacity is a matter of direct practical importance. There are many conditions of service under which metals are subjected to the effects of vibrations set up by resonant conditions, e.g. automobile and aero-engine crankshafts, propeller and turbine blades, parts of aeroplane structures and overhead wires acted on by a wind. In all these applications the damping capacity of the metal employed has an important influence on the life of the part and is being taken into account to an increasing extent. As damping capacity depends on plastic strain a high damping capacity is usually associated with ductility. Consequently metals with a high damping capacity have a low notch-sensitivity and a low endurance limit as determined on plain polished surfaces. To some extent the choice of a material with a high damping capacity involves the use of one with a lower endurance limit, and the problem is to decide how much endurance, as determined on a plain polished specimen, should be sacrificed in order to obtain high damping and low notch-sensitivity. The relations between damping on the one hand and ductility and endurance limit on the other are not very definite, however, and consequently it will probably be found when more work has been done that among the metals and alloys available there are wide differences in the damping capacities associated with a given endurance. Förster and Köster place the pure metals in the order of diminishing damping capacity as follows: nickel, tin, lead, copper, cadmium, iron, magnesium, and aluminium. This is not in the order of increasing endurance limit nor decreasing ductility, and damping capacity is evidently not directly related to either of those properties.

Experimental Investigation of Changes during Fatigue Tests.

The foregoing account of the mechanism of fatigue is based on the results obtained in a number of investigations on deformation under

repeated cycles of stress. In these, four methods of observing deformation have been used: (1) measurement of changes in length by means of extensometers, (2) measurement of changes in temperature by means of thermo-couples, (3) observation of slip-bands by means of a microscope, and (4) X-ray analysis.

Bauschinger (167) was the first to investigate stress-strain relations during repeated cycles of stress by means of an extensometer, and thirty years later the work was continued by Bairstow (166) who studied the stress-strain loops and the total permanent extension produced by cycles of reversed and other types of stress. Since then the method has been used by several investigators including Gough and Hanson (169), Gough (170), and Hankins (171). In the first of these investigations Armco iron was studied, and it was found that under a range of stress less than the limiting range, the hysteresis loop which was wide at first quickly attained a minimum value and remained unchanged for 30 million cycles. Similar results were obtained by Gough with copper. Large hysteresis loops were first obtained, but these decreased with repeated applications of a safe range of stress, until after 407,000 cycles the metal attained a reversible condition. After 2,812,000 cycles the loop was unaltered, thus showing that under the repeated application of a safe range of stress a metal that exhibits no range of elasticity in static tests becomes reversible within the range of stress employed.

The method of estimating cyclical deformation by means of thermo-couples attached to the specimen depends on the fact that when permanent deformation is taking place heat is evolved in sufficient quantities to cause a marked rise in the temperature of the metal, whereas, when the extension and contraction are reversible, the evolution of heat due to hysteresis is relatively small. Thus when a metal is subjected to cycles of stress that produce considerable amounts of slip a comparatively large evolution of heat takes place. This is known as a 'heat-burst'. If the range is a safe one, the rate of evolution of heat diminishes as a result of the progressive decrease in the amount of deformation per cycle. If the applied range of stress just exceeds the limiting range, the rate of evolution of heat may decrease until it almost equals that due to reversible plastic strain, but later, when the fatigue cracks appear, it again increases rapidly until the specimen fractures. This method has been applied to the study of fatigue by Hopkinson and Williams (172), Rowett (173), Stromeyer (174), and Hankins (171).

Microscopic observation of specimens undergoing fatigue tests cannot conveniently be carried out continuously during the test. As the effects observed by the microscope are permanent, however, this does not detract from the importance of the method, which provides a direct means of determining the extent to which slip is taking place. The other methods of studying the mechanism of fatigue do not provide direct evidence on the nature of the changes taking place in the metal,

and although inferences may be drawn from them the present conception of the behaviour of metals under repeated cycles of stress ultimately rests on the results obtained by the microscopic observation of slip-bands appearing at the surface.

Ewing and Rosenhain (175) were the first investigators to study slip-bands and to appreciate their significance. Later on, Ewing and Humfrey (176) applied the microscope to the study of fatigue, and this was continued by Stanton and Bairstow (177) and Gough and Hanson (169). These last investigators studied the changes in microstructure of Armco iron, several steels, copper, &c., under safe and unsafe ranges of stress, including alternating and repeated direct stresses, reversed bending stresses, and reversed torsional stresses. Their principal observations on slip-bands were as follows:

- (a) Slip-bands were found to result from ranges of stress considerably lower than the limiting range.
- (b) No marked difference could be detected between the slip-bands due to safe or unsafe ranges.
- (c) Concentrations of slip-bands, which appeared under lower magnification as broad dark bands, but which could be resolved into masses of fine slip-bands at high magnification, were observed under safe and unsafe ranges of stress.
- (d) The fatigue cracks originated in areas of heavy slip, but they spread indiscriminately through areas of heavy slip and areas free from previous slip.

When large single crystals prepared by the methods developed by Carpenter and Elam and Bridgman became available, an extensive study of fatigue phenomena in single crystals was started by Dr. Gough at the National Physical Laboratory. The results obtained in this investigation in the period 1923-33 are reviewed by him (26), and in this lecture references are given to the separate papers published during this time. These results are in accordance with what has already been said about the mechanism of fatigue, and much of what has been said is actually based on them, but in Dr. Gough's lecture and the papers on which it is based the subject is considered in much greater detail than is possible here. From experiments on single crystals, specimens consisting of two large crystals, and ordinary polycrystalline metals, it was concluded that the mechanism of fatigue was the same in all cases, and that failure resulted from the propagation of cracks formed in the first instance in regions where considerable amounts of slip had occurred. Thus the cause of fatigue failure is the change in the crystal structure produced by slip and associated with strain-hardening. Repeated cycles of stress can produce the condition necessary for the initiation of cracks because slipping continues during repeated cycles. It is not the number of slip-bands produced in the specimen as a whole that leads to eventual failure, but the amount of slip and consequent change in crystal structure that

occurs in certain regions. The endurance limit depends on the fact that the effect of a given range of stress in producing slip diminishes with each cycle until a certain number has been applied, then the amount of reversible plastic strain produced during each cycle remains constant, and if it is enough to produce a certain amount of strain-hardening the metal eventually fractures, whereas, if it is not, the metal lasts indefinitely. It does not necessarily follow that visible slip-bands should still be appearing when the cracks first begin, and under certain conditions there may be a considerable lag between the apparent cessation of slip and the detection of cracks. During this period, however, some change must still be proceeding in regions of previous slip, and for part of the time the principal change will be extension of cracks from sub-microscopic dimensions.

Fatigue cracks have their origin in regions where considerable amounts of slip have taken place leading to the formation of broad bands consisting of numerous individual slip-bands. In these regions (and probably in all others where slip has occurred) discontinuities in crystal structure are produced by slip, and it is the extension of these under repeated cycles of stress that gives rise to fatigue cracks. When they first appear fatigue cracks tend to follow the slip-planes, but later their course is determined by the path of least resistance to the external applied forces. Thus under direct cycles of stress the plane of propagation of fatigue cracks and of ultimate fracture is normal to the axis of stress. Crystal boundaries tend to retard the propagation of cracks, but they have no influence on their path which may cross boundaries without any change in direction. Thus, in general, once a fatigue crack is properly established, its direction of propagation is controlled by the applied forces and is not affected by crystal boundaries or crystallographic planes.

X-rays have also been used to study the more subtle changes produced in metals by repeated stress. This work has shown that the changes produced by repeated stress closely resemble those produced by static stress. These changes are described briefly in Chapter III in the section on 'Phenomena Associated with Slip'. In this connexion considerable importance is attached to the question whether the ultimate changes in crystal structure produced by an unsafe range differ from those produced by a safe range. This problem has been extensively investigated and the subject is reviewed by Barrett (592) who concludes that X-ray analysis is not able to show whether a range of stress is safe or unsafe. In more recent work, however, Gough and Wood (591) reach the opposite conclusion.

CORROSION-FATIGUE

Metals in service are exposed to a variety of environments of which the most common are the atmosphere, natural waters, steam, and

furnace gases. The noble metals gold, platinum, &c., are inert towards these environments, but when the common metals iron, copper, lead, tin, nickel, zinc, aluminium, magnesium, and their alloys are exposed to them, some chemical reactions between the metal and the environment occur. Under certain conditions the result of the reaction between the clean surface of the metal and the environment is the production of a film that protects the metal from further attack. Under others the reaction proceeds and the metal is progressively converted into some compound which has neither the properties nor the appearance of metal. In these reactions two different kinds of processes are involved and are known respectively as electrochemical corrosion and direct oxidation. In the former an electrolyte is required, and this type of action can only occur when water has access to the surface of the metal as a result of immersion, exposure to rain, condensation or absorption by some hygroscopic substance in contact with the metal. When these conditions are not realized the chemical action that occurs is direct combination between the metal and the atmosphere to which it is exposed. In both processes the reaction at the surface of the metal may lead to the formation of a film that is highly impermeable to ions in the case of electrochemical corrosion or gas molecules in the case of direct oxidation. Such films protect the metal against further attack, and as the mechanism of formation and the properties of the films produced in the two processes are similar, a film formed in one way gives protection against either kind of attack. Similarly, in both processes the reaction may be progressive and result in the gradual decay of the metal. The mechanism of the progressive attack is different in the two cases and its rate is controlled by different factors.

Direct combination between the common metals and oxygen or other gas takes place slowly and only to a limited extent at atmospheric temperature, and the decay of metals at this temperature is mainly due to electrochemical corrosion. The rate of direct oxidation and the extent to which it proceeds increase with the temperature, whilst electrochemical corrosion does not take place at temperatures above that at which water can exist as a liquid. At elevated temperatures direct oxidation is therefore the phenomenon that has to be considered in connexion with the decay of metals. These two processes that cause the decay are fully considered in the next chapter, and for the present purpose both may be considered to be covered by the term corrosion. In general, therefore, corrosion-fatigue means a combination of corrosion and fatigue and the corrosion may be either electrochemical or direct oxidation. Most of the interest in corrosion-fatigue has been confined to conditions involving electrochemical corrosion, but similar effects may arise under conditions involving direct oxidation.

When the ordinary industrial metals and alloys resist corrosion it is because under the conditions of exposure a continuous oxide film impervious to the corroding medium is formed on their surface. When

all the solids, liquids, and gases with which metals come into contact are considered, it is found that a metal that has a high resistance to some substances may have a low resistance to others, but in so far as the ordinary media are concerned some metals may be generally classified as highly resistant to corrosion and others as very susceptible to it. The metals in the resistant class are those that readily form protective films, e.g. stainless steel, nickel-copper alloys, bronze, aluminium-bronze, and pure aluminium, while those in the susceptible class are carbon steels, alloy steels (other than stainless steels), cast iron, and brass. Ferrous metals other than the stainless varieties are particularly susceptible to corrosion and unless specially protected will be attacked in moist atmospheres or when immersed in water. When corrosion takes place the cross-sectional area is reduced either uniformly or irregularly and pits are formed on the surface of the metal. As a result, the static strength is decreased, and when the marked effect of surface irregularities on endurance is considered it is not surprising that the resistance to fatigue is diminished to an even greater extent. The corrosion may occur before the metal is subjected to repeated stress, or fatigue and corrosion may proceed simultaneously, but in either case a decrease in endurance would be expected from consideration of the visible change in the metal and the known effect of surface condition on fatigue.

In recent years great interest has, however, been aroused by the realization that when metals are subjected to chemical attack while repeated stress is being applied, the results obtained are not what would be expected from a consideration of the separate phenomena of corrosion and fatigue. When these take place at the same time the reduction in fatigue resistance is in many cases much greater than would be expected from the amount of corrosion that has occurred. The phenomena are therefore mutually accelerative, and as the endurance properties of a metal may be seriously impaired, although the visible evidence of corrosion is slight or entirely absent, it is apparent that the combined effect of fatigue and corrosion leads to the realization of some new conditions of failure. It is this that is specifically meant by the term corrosion-fatigue.

Attention was first directed to the phenomenon of corrosion-fatigue by the work of Haigh in 1917 (178). In an investigation of the endurance properties of brass he tried the effect of immersion in corrosive solutions both before and during testing. A specimen of Muntz metal (60 Cu 40 Zn) was immersed in ammonia, washed, dried, and subjected to a fatigue test. Its fatigue limit was not affected. Another specimen while undergoing a fatigue test was wrapped in a pad of cotton wool soaked in ammonia. Its fatigue limit was reduced by 10 per cent. Naval brass (62 Cu 37 Zn 1 Sn) was likewise affected by ammonia applied during the test, its fatigue limit being reduced 16 per cent. In 1926 Lehmann (179) published an account of an investigation on the

effect of corrosion-fatigue on two carbon steels subjected to the action of various solutions. He found that the fatigue limit of 0.33 per cent. carbon steel was not affected by contact with sodium nitrate, sodium chloride, or lubricating oil, but that it was reduced 5 per cent. by contact with distilled water and hot sodium nitrate and 21 per cent. by contact with hot ammonium chloride. About the same time McAdam (180) published a report on the lowering of the fatigue limit when specimens were tested in a stream of water. He introduced the term corrosion-fatigue and extensive interest in the subject dates from this time. During the intervening period many investigations have been carried out mainly by McAdam and by investigators working on behalf of the Aeronautical Research Committee of the Air Ministry. The position of the subject in 1932 was reviewed by Gough (181).

McAdam observed that the S/N curve for specimens immersed in water passed below the curve for specimens tested in air. At a sufficiently high number of reversals it seemed to become horizontal, thus indicating the existence of a corrosion-fatigue limit which it appeared could be ascertained in tests extending to 10^8 reversals. Later work by McAdam and others has shown that the earlier view that the S/N curve becomes horizontal about 10^8 cycles is not generally true, so that even when everything is constant except range of stress and number of cycles it cannot be said that below a certain range of stress failure will not occur. Thus even for constant conditions there is no corrosion-fatigue limit comparable with the fatigue limit revealed in tests on steel at atmospheric temperature. This arises from the fact that corrosion proceeds with time irrespective of other conditions, and the corrosion-fatigue limit for constant conditions is simply an arbitrary quantity indicating the range of stress that will be withstood for a stated number of cycles under those conditions. If the corroding medium is changed, the corrosion-fatigue limit on a basis of N cycles is altered so that for each set of conditions a different limit must be determined. Thus in dealing with corrosion-fatigue there is no quantity comparable with the fatigue limit of steel at atmospheric temperature under reversed stresses that can be used in comparing one material with another.

As an illustration of the effects of corrosion-fatigue some experiments carried out by McAdam may be described briefly. These were performed under one set of conditions, i.e. the stresses were reversed bending applied in a rotating-cantilever machine at a frequency of 1,450 cycles per minute and a stream of water was directed on the specimens during the tests. The corrosion-fatigue limit was taken as the point at which the S/N curve appeared to become horizontal or as the longest endurance investigated. The number of cycles on which the limit is based therefore varies, but the results are sufficiently comparable for the present purpose. In one set of experiments McAdam compared the effect of immersion in water before testing with that of immersion for different periods of time during the test. Some of his results for the

corrosion-fatigue limit of a 0.36 per cent. carbon steel in water are given below as percentages of the endurance limit in air:

100,000 reversals in water, then in air to failure	80%
300,000 " " " "	67%
1,500,000 " " " "	51%
1,500,000 reversals in water without load, then tested in air to failure	

These results show clearly that simultaneous fatigue and corrosion have a marked effect which is much greater than that of corrosion in the same medium for the same time followed by testing in air.

In another series of experiments the corrosion-fatigue limits in fresh and salt water of a number of materials in different conditions were compared with each other and with the endurance limit in air. The materials investigated included a number of carbon and alloy steels, stainless steels, nickel-copper alloys, aluminium alloys, &c. The carbon steels varied in composition from 0.03 to 1.09 per cent. of carbon. They were tested in different conditions of heat treatment. Their tensile strengths varied between 19 and 50 tons per sq. inch, and their endurance limits between ± 9.4 and ± 23.6 tons per sq. inch. Yet their corrosion-fatigue limits in fresh water all lay between ± 6.7 and ± 11.2 tons per sq. inch, thus indicating that the increase in strength obtained by heat treatment and higher carbon did not have much effect on the corrosion-fatigue limit although it raised the endurance limit considerably.

A quenched and tempered nickel steel with a tensile strength of 55.7 tons per sq. inch and an endurance limit of ± 30.8 tons per sq. inch had a corrosion-fatigue limit of only ± 11.2 tons per sq. inch. A group of nickel-chromium steels in different conditions of heat treatment gave tensile strengths between 41 and 66 tons per sq. inch and endurance limits between ± 21.8 and ± 32.6 tons per sq. inch, yet their corrosion fatigue limits were all between ± 12.1 and ± 12.5 tons per sq. inch. These results provide further evidence that the effects of varying composition and heat treatment in increasing the fatigue limit are almost entirely eliminated when corrosion takes place at the same time as fatigue.

Although the mechanical properties of steel are greatly affected by alterations in composition and treatment their resistance to corrosion is not influenced to such a marked extent, and it appears from the results quoted above that it is not mechanical strength but resistance to corrosion that determines the corrosion-fatigue limit. This conclusion is supported by the results obtained by McAdam on steels of the stainless class. In these steels a high resistance to corrosion is obtained principally by the addition of chromium in amounts exceeding 12 per cent. and to a lesser extent by the further addition of nickel. The behaviour of a series of these steels containing from 11.5 to 14 per cent. of chromium and 0.08 to 0.33 per cent. of carbon was not very satisfactory. Their average endurance limit was ± 21.6 tons and their average corrosion-fatigue limit ± 15.2 tons. A series of stainless steels

containing between 8 and 34 per cent. of chromium and 5 and 17.7 per cent. of nickel gave much better results. Their average endurance limit was ± 23.9 tons, and their average corrosion-fatigue limit ± 19.6 tons. It appears therefore that although methods of increasing mechanical strength and endurance limit do not raise the corrosion-fatigue limit, increased resistance to corrosion has the requisite effect.

Whereas the endurance of a given specimen subjected to a fatigue test in air at room temperature under reversed bending stresses is determined almost entirely by the range of stress, the resistance to corrosion-fatigue under similar conditions except for corrosion is influenced by the nature of the corroding medium, the corrosion resistance of the metal, the frequency of the stress cycle, and time. Thus, even when variations in mean stress and temperature are disregarded, the investigation of the corrosion-fatigue properties of a given metal in a particular condition is a complicated matter involving consideration of the corroding medium, range of stress, frequency of cycle, and time. In order to obtain a measure of the damage done to the fatigue resistance of specimens by different conditions of corrosion-fatigue McAdam adopted the method of subjecting them to corrosion-fatigue under different conditions followed by a determination of their fatigue limits in air. In the first stage the corroding medium, the range of stress, the number of cycles, and the frequency were varied separately. The second stage was simply a test to discover how much damage had been done to the endurance during the first stage, and by comparing the fatigue limit obtained in this second stage with that of fresh uncorroded specimens a measure of the damage done was obtained. The experiments carried out by McAdam were published in a series of ten papers and the results are summarized by Gough (181). A few of these may be mentioned here.

In one series of experiments a number of metals were subjected to different ranges of stress in the first stage while the other conditions were kept constant, i.e. number of cycles (20×10^6), frequency of cycles (1,450 per minute), corrosion time (10 days), and environment (stream of carbonate water in air). In the case of carbon steel, nickel steel, and chromium-vanadium steel the fatigue limit in the second stage was found to decrease rapidly with increase in the range of stress applied in the first stage. In the case of duralumin, stainless iron, Monel metal, and aluminium-bronze the fatigue limit in the second stage was not greatly affected by the range of stress applied in the first stage, i.e. it was not appreciably lowered by the corrosion-fatigue. In another series of experiments the range of stress, the frequency, and the time of exposure (i.e. number of cycles divided by frequency) were varied in the first stage. Curves were plotted showing the fatigue limit in the second stage against the duration of the first stage, each curve applying to a constant frequency and range of stress. The metals studied were found to fall into two classes represented respectively by nickel steel

and Monel metal. In the case of nickel steel all the curves were of the same shape, i.e. when the endurance limit in the second stage was plotted against the duration of the first stage (for constant frequency and range of stress) the endurance limit first fell rapidly and then more slowly as the duration increased. This result was obtained even when the range of stress applied in the first stage was zero, and as the range of stress applied in the first stage increased (duration and frequency constant) the endurance limit in the second stage decreased progressively. For a constant range of stress and a constant duration in the first stage the endurance in the second stage increased as the frequency decreased. For nickel steel and other readily corrodible metals, e.g. carbon and ordinary steels generally, it may be said that the damage caused by corrosion-fatigue in a given medium increases with the range of stress, the duration of the test, and the frequency of the stress cycles. In the case of Monel metal the endurance in the second stage decreased slightly with increase in the duration of stressless corrosion in the first stage. When a range of stress was applied in the first stage the endurance in the second stage fell slowly with increase in the duration of the first stage, until after a certain duration it began to fall very rapidly. As the range of stress was increased the time required to reach the stage at which a rapid decrease in endurance began was decreased, and the same result was obtained when the frequency was increased. Monel metal thus resembled nickel steel in that the damage caused by corrosion-fatigue increased with the range of stress, the duration of the test, and the frequency of the stress cycles, but it differed in that the effect of these was not progressive. Thus up to a certain range, frequency, and duration the effect of corrosion fatigue was small, beyond this it was very pronounced.

The essential feature of corrosion-fatigue is that the repeated stress increases the capacity of the corrosion medium for producing small sharp pits and these in turn provide starting-points for fatigue cracks and thus decrease endurance. The preferential corrosion induced by the repeated stress takes place on the slip-bands, and it is there that deep sharp pits that subsequently become cracks are formed. These cracks are propagated in the first instance along the slip planes but at later stages their paths are similar to those of ordinary fatigue cracks and are not influenced by crystallographic planes or crystal boundaries. In the case of ordinary steels and other metals susceptible to corrosion, the effect of corrosion-fatigue is progressive, i.e. the endurance decreases with increase in the corrodibility of the medium, the range of stress, the frequency, and the duration of the test. In the case of stainless steels, Monel metal, and other corrosion-resistant metals the effect of corrosion-fatigue is not so definitely progressive, and unless a certain critical combination of corrodibility, range of stress, and frequency is exceeded the effect is small, whereas when it is exceeded the effect is pronounced. It is here that the mutual relations of repeated stress and

protective film formation become important. All the common corrosion-resisting metals owe their resistance to the readiness with which protective films are formed by a reaction between the metal and its environment. When such a metal is subjected to the action of repeated stress in a medium in which such films can form, two opposing factors come into operation. On the one hand the contraction and expansion of the metal and the formation of slip-bands tends to crack the films, while on the other the reaction between the metal and the environment tends to keep them in repair. If the latter process predominates, the effect of the corroding medium is small; if the former predominates, the effect of the corroding medium is large, i.e. if the film is not kept in repair corrosion takes place at the fissures, and sharp pits which later become fatigue cracks are formed.

As the endurance of metals is affected by their environment and as air is not without effect on metals, it follows that in tests made in air the influence of corrosion is not completely absent. To discover the extent of this influence Gough and Sopwith (182) carried out a series of tests in air and in a vacuum of 10^{-3} mm. of mercury. Some of their results are given in Table 42, from which it will be seen that the fatigue limit *in vacuo* is, in general, slightly higher than that in air, while in the case of copper and brass it is considerably higher, viz. 14 and 26 per cent. respectively.

TABLE 42

Material	Fatigue limits, tons per sq. in.		Ratio B/A
	A In Air	B In Vacuo	
0.5% C steel (cold-rolled) . . .	± 21.75	± 22.5	1.03
Stainless steel (Cr 15 C 0.12) . . .	± 22	± 22.25	1.01
Stainless steel (Cr 18 Ni 8 C 0.1) . . .	± 24.75	± 24.25	0.98
Stainless steel (Cr 17 Ni 1 C 0.25) . . .	± 28.25	± 28.25	1.00
Duralumin	± 7.75	± 8.25	1.06
Magnesium alloy (2.5% Al)	± 5.5	± 5.5	1.00
0.13% C steel	± 13.0	± 13.7	1.05
Copper (99.96%) annealed	± 4.3	± 4.9	1.14
Brass (70:30) annealed	± 7.2	± 9.1	1.26

CHAPTER VIII

OXIDATION AND CORROSION

Introduction.

IN manufacturing operations and service applications metals come into contact with a large variety of solids, liquids, and gases, and the way in which they react to these is an important factor in their treatment and use. The metals employed in industrial chemical plant and in the manufacture and handling of food have to resist the chemical action of many substances, but the environments to which metals are most commonly exposed are the atmosphere, natural waters, steam, and furnace gases. In general, therefore, in considering the chemical properties of solid metals it is these environments that are taken into account and the effects of other environments are regarded as special cases. The noble metals gold, platinum, &c., are inert towards the ordinary environments, but when the common metals copper, lead, tin, nickel, iron, zinc, aluminium, magnesium, and their alloys are exposed to them some chemical reactions occur. Under certain conditions the result of the reaction is the production of a film that protects the metal from further attack. Under others the reaction proceeds and the metal is progressively converted into some compound which has neither the appearance nor the properties of metal.

In these reactions between metals and their environments two different kinds of processes are involved. These are known respectively as electrochemical corrosion and direct oxidation. In the former an electrolyte is required, and this type of action can only take place when water has access to the surface of the metal as a result of immersion, exposure to rain, condensation, or absorption by hygroscopic substances in contact with it. When these conditions are not realized the chemical action that occurs is direct combination between the metal and the atmosphere to which it is exposed. In both processes the reaction at the surface of the metal may lead to the formation of a film that is highly impermeable to ions in the case of electrochemical corrosion or to gas molecules in the case of direct oxidation. Such films protect the metal against further attack, and as the mechanism of formation and the properties of the films produced in the two processes are similar, a film formed in one way gives protection against either kind of attack. Similarly, in both processes the reaction may be progressive and result in the gradual decay of the metal. The mechanism of progressive attack is different, however, in the two cases and its rate is controlled by different factors.

Direct combination between the common metals and oxygen or some other gas takes place slowly and only to a limited extent at atmospheric temperature. The decay of metals at temperatures close to

atmospheric is therefore mainly due to electrochemical action. In general, however, the rate of direct oxidation and the extent to which it proceeds increase with the temperature, while electrochemical corrosion does not take place at temperatures above that at which water exists as a liquid. At elevated temperatures direct oxidation is therefore the more important phenomenon. As most metal-work is kept at atmospheric temperature during use, electrochemical corrosion functions chiefly in connexion with the behaviour of metals in service. Most of the treatments performed in the preparation of metals for use involve heating, and consequently, direct oxidation is principally operative in connexion with treatment and is only of importance in relation to service when the metal is used at elevated temperatures.

General Aspects of Direct Oxidation.

When specimens of the common metals are cleaned by abrasion and exposed to the atmosphere at ordinary temperature under conditions that preclude condensation or deposition on the surface of hygroscopic particles, direct oxidation occurs. In the initial stage of the process the surface layer of metal atoms combines with oxygen and a layer of oxide one molecule thick is produced. If this layer is discontinuous oxygen can penetrate to the underlying metal and combine with it, and consequently, as long as it remains discontinuous oxidation can proceed at about the same rate as it began. If, however, the oxide layer initially formed is continuous and free from cracks, the surrounding atmosphere does not have direct access to the underlying metal. In such a case if oxidation is to continue it must do so in one of the following ways:

1. Oxygen dissolves in the oxide film and diffuses through it to the oxide-metal interface where it combines with the metal.
2. Metal dissolves in the oxide film and diffuses through it to the oxide-gas interface where it combines with oxygen.

In general, therefore, when a freshly abraded metal surface is exposed to the atmosphere at ordinary temperature the subsequent behaviour depends firstly on whether the metal combines with oxygen or not, secondly on whether any oxide layer formed is continuous or not, and thirdly, when a continuous film is formed, on the rate of diffusion of oxygen or/and metal through this film.

When gold and platinum are exposed to the atmosphere at ordinary temperature no reaction takes place. When copper, lead, tin, nickel, cobalt, iron, chromium, and aluminium are similarly exposed combination between oxygen and the metal surface occurs, but as the oxide film is continuous and diffusion through it is extremely slow the rate of oxidation decreases rapidly with time. Under similar conditions, however, zinc, magnesium, and calcium form a discontinuous oxide film and oxidation proceeds at the initial rate which, however, is comparatively slow.

When reactive gases such as hydrogen sulphide or hydrogen chloride are present in the atmosphere they influence the structure of the continuous films, and even at atmospheric temperature these may continue to grow until an appreciable thickness is attained. As the temperature is raised combination between metals and oxygen takes place with greater facility, and the metals on which discontinuous oxide layers are formed undergo rapid oxidation. In the case of metals on which continuous films are formed the initial rate of oxidation increases with the temperature. On some of them, e.g. aluminium and chromium, the film remains highly resistant to diffusion and thickens either slowly or not at all. On others, e.g. copper and iron, the rate of diffusion in the oxide increases with the temperature. The films have therefore to become considerably thicker before the rate at which oxygen reaches the metal or metal reaches the atmosphere becomes negligible, if it ever does. This increase in thickness is accompanied by a greater tendency to crack, and films cannot remain continuous when their thickness exceeds a certain limit. The metals that have the greatest resistance to oxidation at elevated temperatures are those which form oxide films that exhibit the highest degree of impermeability to oxygen. In other words resistance to oxidation is only obtained when under the conditions of exposure a film is formed that becomes substantially impervious to gas and diffusion of metal while still quite thin. Should such a film be broken or rubbed off it is healed by further oxidation of the metal.

The films formed on metals exposed to air at atmospheric temperature are usually too thin and transparent to be visible while on the metal, but, as shown later, their formation has been proved in several ways. The thicker films formed at higher temperatures are also transparent, but, as explained later, they are visible on the metal because of interference colours. If, however, the nature of the metal and the time and temperature of exposure are such that growth of the oxide layer continues, it eventually becomes opaque and displays its characteristic colour. Invisible films and interference colour films are in general protective, and it is because of them that metals like aluminium, stainless steel, and nickel alloys remain unaffected by exposure to the atmosphere. When, however, the rate of diffusion in the oxide is such that progressive oxidation takes place at an appreciable rate, then oxidation becomes a serious problem in the use and treatment of metals.

Three principal aspects of direct oxidation may be distinguished: (1) the mechanism and rate of oxidation, (2) the relation of oxidation to the use of metals, and (3) the relation of oxidation to the treatment of metals. The object of the study of (1) is to obtain information bearing on the relations between the individual metals and alloys on the one hand, and time, temperature, and atmosphere on the other, in so far as these factors influence the way in which oxide layers are produced, the rate at which they are formed, and the composition, con-

stitution, structure, and properties of the resulting oxide. It is clear that in such a study many factors are involved and they can be divided into three groups as follows:

A. Factors relating to the metal.

These include in the first place the different behaviour of the different metals iron, copper, aluminium, nickel, chromium, &c. Secondly, they include the effects of the addition to the basis metals of suitable alloying elements in different amounts and combinations.

B. Factors relating to the conditions of exposure.

These include time, temperature, and the composition and pressure of the atmosphere.

C. Factors relating to the oxide.

These include the difference between discontinuous and continuous oxide layers, and changes in the oxide due to cracking and sintering, i.e. a transformation in the oxide layer that results in a decrease in the rate of diffusion through it. They also include the composition, constitution, and structure of the oxide.

In most cases of oxidation many of these factors have to be taken into account at the same time.

Two aspects of the relations between oxidation and the use of metals may be distinguished, namely (1) the consequences of oxidation in use, and (2) the prevention of oxidation in use. The consequences are obvious, for if a metal is used under conditions that produce progressive oxidation its effective section will eventually be reduced below that required to withstand the applied stresses, and failure will follow. The prevention of oxidation in use depends on (a) the selection of a metal that will withstand the imposed conditions without undergoing progressive oxidation at an appreciable rate, and (b) the protection of oxidizable metals with surface layers of non-oxidizable metals or other substances. In selecting metals that will withstand the imposed condition account must be taken of cost, melting-point, and mechanical properties in addition to rate of oxidation. In general, the greatest resistance to progressive oxidation at an appreciable rate is displayed by the more expensive metals, and although high resistance to progressive attack under most conditions of service may be obtained by the selection of the appropriate metal, consideration of cost frequently leads to the use of metals under conditions where they are liable to fairly rapid oxidation. The metals tin, lead, and zinc melt at 232°, 327°, and 420° C. respectively, and as their mechanical strength at ordinary temperature is low, and becomes zero at the melting-point, they are not suitable for use at elevated temperatures in spite of the fact that the resistance to oxidation of solid tin and lead is considerable. Although these metals and the alloys based on them are not suitable for applications at elevated temperature, tin and zinc, when added to copper, increase its resistance to oxidation, although not to the same extent as nickel, aluminium, or silicon. Aluminium melts at 660° C., it has a remarkable

resistance to oxidation, and although the metal itself is soft some strong alloys are based on it. Certain of these alloys, e.g. those used for pistons, are suitable for use at temperatures up to 350°C . Copper, nickel, and iron melt at $1,083^{\circ}$, $1,440^{\circ}$, and $1,532^{\circ}\text{C}$. respectively. From this point of view they are all suitable as the basis of alloys for use at elevated temperature. At atmospheric and elevated temperatures copper is much softer than the other two, and the use of copper base alloys at elevated temperatures is limited to the range of temperature in which they retain an appreciable strength. For service at higher temperatures only iron and nickel base alloys are, in general, available. Neither of these metals is suitable for use at high temperatures in the pure state, and all the heat-resisting materials are alloys. Some of the constituents used in these are added to increase the strength at elevated temperature. Of those used to augment resistance to oxidation, aluminium, chromium, and silicon are the most widely employed. Heat-resisting alloys consist of two groups, based on iron and nickel respectively, the principal alloying elements in each case being the three elements just mentioned.

The oxidation of metals in manufacture may have a pronounced effect on their behaviour in use. Thus the oxidation of steel during hot-working produces decarburization and surface irregularities which decrease the resistance of the material to repeated stress. Furthermore, the rolling scale remaining on steel reduces its resistance to electro-chemical corrosion. Oxidation, however, has also an important effect on the preparation for use and this may be discussed under two heads, namely Consequences and Prevention.

Numerous consequences follow from the oxidation of metals during the processes applied to them in manufacture. These include heating prior to hot-working, hot-working, cold-working, intermediate annealing, final annealing, quenching, and tempering treatments. All of these except cold-working involve heating and the consequences arising from oxidation. The temperatures reached in heating in preparation for hot-working are the highest to which the solid metals are exposed. In the case of steel the rate of oxidation at these temperatures is so great that a considerable amount of metal is lost. In addition to this the oxide that drips or flakes off the heated steel reacts with the refractory lining of the furnaces and tends to destroy it. In drop-forging, scale adhering to the metal causes it to stick to the dies, some of it may be forced into the metal and cause difficulties in machining, while owing to its abrasive action it decreases the life of the dies. Most of the scale formed during heating is broken off during hot-working, but fresh scale is formed while the metal is being worked, and a considerable amount of labour is expended in loosening and clearing this off.

At the end of the hot-working operations metals that are susceptible to oxidation at the forging temperatures are covered with scale. A considerable amount of steel goes into service with this still adhering. For many purposes, however, it must be removed, and this applies, in

general, to the non-ferrous metals. This removal of the scale is accomplished by 'pickling' and the metal is then ready for cold-working or other operations. When the amount of cold-working that has to be performed to effect the necessary change in shape or dimensions is such that intermediate annealing is necessary, further oxidation occurs, and this necessitates 'pickling' after each annealing. If the metal is finally annealed at the end of the cold-working operations it must again be 'pickled' if a bright surface is required.

In the quenching and tempering operations performed on the non-ferrous metals, temperatures that produce rapid oxidation are not reached. But in the heating of steel for quenching, oxidation is a serious problem. When steel is to be used in the hard condition, it is necessary to machine the parts to the required dimensions before quenching. Any oxidation that takes place during heating for hardening then becomes important as it leads to a change in dimensions. Furthermore, the presence of oxide on the surface of articles that have to be quenched in water, oil, salt, or molten metal may seriously retard the cooling. From this point of view thin scales are a greater disadvantage than thick ones for they adhere tenaciously to the metal and do not split off on quenching. Frequently, although most of the scale flakes off on immersion, small pieces cling to the part, and as the metal under these is not properly quenched 'soft spots' are the result.

Oxidation during manufacture probably gives rise to more difficulties than oxidation in use, for the latter can be to some extent avoided by the selection of suitable materials, whereas the operations employed in the former involve the heating of readily oxidizable metals to a high temperature. Even the heat-resisting materials may undergo a troublesome amount of oxidation in this way, for the temperatures reached are higher than those to which the metal will be subjected in service, and oxide films that would be protective in service must be removed from metals that have to undergo cold-working operations.

Because of the numerous disadvantages of oxidation in heating operations a considerable amount of attention has been devoted to methods of restricting or preventing its incidence. These vary from limiting the air supplied to fuel furnaces and providing atmospheres of half-burnt gas in electric furnaces to heating in salt baths and in artificial atmospheres of nitrogen and hydrogen. These latter methods are at present only used in the heat treatment of expensive metals or of small parts that are heated after being machined to size. In most metallurgical operations it is necessary to restrict oxidation either by controlling combustion so as to produce an atmosphere that is neutral or reducing or by packing the heated parts in boxes along with materials that will produce reducing conditions.

If no artificial atmosphere is provided the atmosphere in electric furnaces consists of air. In fuel-fired furnaces it consists of the products of combustion sometimes mixed with excess air or excess fuel. The

principal constituents of primary fuels such as coal, natural gas, and oil are carbon, hydrogen, and hydrocarbons. Producer gas contains large quantities of carbon monoxide. All these constituents are reducing. In combustion they combine with air to form carbon dioxide and water vapour. These gases are oxidizing, and as excess air is required for complete combustion the furnace atmosphere resulting from efficient combustion is strongly oxidizing. To reduce the oxidizing power of the atmosphere the air supply is restricted so that instead of excess air the furnace gases contain carbon monoxide and hydrogen mixed with the carbon dioxide and water vapour. The production of such an atmosphere involves inefficient combustion, and in arranging the conditions of heating account must be taken of fuel costs and the heat required as well as of the prevention of oxidation. In electric furnaces, oxidation is restricted or prevented by providing an atmosphere of partly burnt gaseous fuel, i.e. a similar atmosphere to that obtained in a gas or oil-fired furnace when the air supply is considerably reduced. In these furnaces, however, atmospheres of nitrogen, &c. may be produced when required (Chapter X).

General Aspects of Electrochemical Corrosion.

There are many applications of metals that depend on the possession of some special property, e.g. the coefficient of expansion, the coefficient of friction, the constancy of elastic properties over a range of temperature, or the magnetic properties. In general, however, the factors that determine their use are cost, mechanical properties, electrical properties, suitability for casting or working, and ability to withstand the chemical action of the environment in which they are used, i.e. to resist oxidation and corrosion. In practically every application of metals the last-named property has to be taken into account, but its importance in relation to the other factors varies greatly. If the special classes of ferrous metals known as the stainless steels and rust-resisting cast irons are left out of consideration, it may be said that the alloys based on iron are the most susceptible to oxidation and corrosion of all the common metals. Nevertheless, they are used to a greater extent than all others put together simply because mechanical properties and cost are, in general, more important than other factors, and therefore control the selection of the metal, which has to be protected from corrosion as far as possible by painting, greasing, or coating with some other metal or compound. When the importance of cost and mechanical properties decreases and that of resistance to corrosion increases, the cheaper non-ferrous metals, such as the alloys of copper and aluminium, replace iron and steel, and as the latter property becomes still more important these are, in turn, replaced by alloys of nickel and stainless steel. Finally, when chemical inertness becomes of paramount importance and all other factors are subordinated to it, the precious metals, e.g. silver, gold, and platinum are used.

When a metal fails to resist completely the chemical action of its environment it means that there is a reaction at its surface which results in some of the metal being converted into a compound which has neither the properties nor the appearance of the metal. This reaction may be either slow or rapid, it may take place uniformly over the surface or only at certain points, and the product of the reaction may either adhere to the surface on which it was formed or else be carried away. Whatever the rate or the distribution of the corrosion three important consequences are liable to follow its progress. Firstly, the effective cross-sectional area is reduced and the margin of safety of stressed parts decreased. Secondly, the metallic appearance is destroyed, and when lustrous surfaces are required recourse must be had to continual cleaning and polishing. Thirdly, in plant and containers used for the manufacture and transportation of chemicals and food, corrosion leads to contamination of the materials by the products of corrosion in addition to the ultimate destruction of the plant.

There are several different aspects of the effects of corrosion on the strength of plant, machines, and structures. If the corrosion is equally distributed over the whole surface and only static stresses are applied, the action may continue for a long time before a dangerous situation arises. Frequently, however, it proceeds by the selective formation and deepening of pits, and furthermore it is liable to be concentrated in certain parts of a structure. Under these conditions a dangerous situation may be reached in quite a short time. When dynamic stresses are applied the danger of fracture as a result of the combined effect of stress and corrosion is greatly increased, but the most conspicuous effect of corrosion is shown in parts subjected to repeated stress. The fracture of metals under the combined action of corrosion and repeated stress is known as Corrosion-Fatigue which was considered at the end of Chapter VII. The outstanding feature of this phenomenon is that in an environment capable of corroding a metal its resistance to repeated stress may be greatly reduced *although no visible corrosion has taken place*.

When it is possible to use a metal that is completely resistant to its environment, no corrosion problem exists. Unfortunately, those possessing the greatest resistance are also the most expensive. Consequently, although metals with a very high degree of stability in the ordinary corroding media, air and water, are available, the ideal conditions just mentioned are only occasionally realized. In general, metals are used under conditions that permit corrosion to take place to a greater or less extent, and their life therefore depends on its velocity under the imposed conditions, and the efficiency of the measures taken to prevent or retard it. These may consist of treatment of the metal before it goes into service or while it is in service. Many of the former methods consist of furnishing a cheap or a strong metal which has a low resistance to corrosion with a coating or covering of a more expensive or a weaker

metal which has a high resistance to corrosion. These coatings may be applied by rolling together sheets of the basis metal and the protecting metal, as in the manufacture of rolled gold, nickel-clad steel sheet, and aluminium alloys covered with pure aluminium. They may also be applied by dipping, as in the manufacture of tin plate and galvanized sheet, by the electro-deposition of such metals as nickel or chromium, by spraying with zinc or aluminium, and in several other ways. Protection against corrosion may also be obtained by producing a film of oxide or phosphate on the metal before going into service. The protective treatments applied during service may be divided into two classes according to whether they are applied to the metal or the corroding medium. Examples of the first class are painting, greasing, polishing, and cleaning, and of the second class, such processes as the treatment of boiler feed water. Whatever method is used some expense is involved. If protective measures are dispensed with or not effectively used even greater expense may be incurred through rapid deterioration of the structures, machines, or plant. In addition to this, inadequate protection against corrosion is liable to have dangerous consequences, for any part of a machine or structure that becomes badly corroded is likely to fail in use. This may be accompanied by loss of life or injuries, and in any case involves delay and the cost of replacement. When all the consequences of corrosion are taken into account the annual wastage that may be attributed to it is very considerable.

In what follows, direct oxidation and corrosion will be considered separately as far as possible. The distinction is easily maintained when dealing on the one hand with metals exposed to air or furnace gases during heat treatment or hot-working, and on the other hand with metals immersed in water or exposed to rain. When dealing, however, with indoor atmospheres at ordinary temperature the two phenomena are liable to overlap. Thus, if the atmosphere remains above the dew-point so that no condensation of moisture occurs, and if no hygroscopic substance is in contact with the metal, then direct oxidation only occurs. If, however, condensation takes place or hygroscopic particles collect on the metal, then electrochemical corrosion will proceed. A similar overlapping arises in the case of steam plant normally exposed to superheated steam (an oxidizing gas) but periodically cooled so that condensation occurs.

DIRECT OXIDATION

The atmospheres to which metals are exposed do not consist of pure air, but contain other gases besides oxygen that are capable of reacting with metal. These reactions have to be considered under the heading of direct oxidation. As the principal distinction between the phenomenon now under consideration and electrochemical corrosion is that the former does not require the presence of water, whereas the latter does, metal-gas reactions might be a more suitable title if it were

not for the fact that this covers numerous effects of gases on metals which have nothing to do with the present subject. Of possible titles direct oxidation is the least confusing, and in a chemical sense it covers all the phenomena concerned, for in chemistry, oxidation is defined as the conversion of a substance representing a lower into one representing a higher stage of combination with oxygen, by the addition either of oxygen or an equivalent electronegative atom or radical.

There is considerable variation in the oxygen affinity of the different metals. At one end of the scale gold does not readily combine with oxygen even in the molten state, whereas at the other end metals like sodium and potassium tarnish rapidly when exposed to air at atmospheric temperature. The common metals iron, copper, aluminium, zinc, lead, nickel, tin, and chromium are all capable of combining with oxygen, but the rate of the reaction and the extent to which it proceeds varies with the metal, the temperature, the nature and properties of the oxide film formed, and the kind of impurities present in the atmosphere. If the metals are oxidized when in the molten condition the oxide formed may either dissolve in the metal, as in the case of copper, which is therefore contaminated with oxide, or it may remain as a film on the surface, as is the case with aluminium, the fluidity of which is largely controlled by it. When solid metals are oxidized, the oxide remains on the surface, and their behaviour when exposed to the atmosphere depends to a great extent on the nature and distribution of the oxide.

Types of Oxide Films.

Oxidation of the clean surface of a freshly abraded metal must begin with combination between oxygen and the surface layer of atoms. An extremely thin oxide layer which is in effect an integral part of the metal surface is thus produced. If the 'unstressed' volume of the oxide is greater than that of the metal from which it is formed the oxide film while on the metal will be stressed in compression in directions parallel to the metal surface. If, however, the 'unstressed' volume of the oxide is less than that of the metal from which it is formed the oxide film while on the metal will be stressed in tension in directions parallel to the metal surface. In the first case release of the stress in the oxide film can be obtained by the formation of cracks and overlapping of the film along the edges of the cracks. In the second case release of stress can result by the formation of cracks and the contraction of the oxide away from them so as to produce discontinuous particles of oxide separated by exposed areas of metal surface.

Cracking cannot occur until the films reach a certain thickness which is greater in the case of those in compression than in that of those in tension. Meanwhile, increase in thickness takes place by diffusion through the film. The thick oxide films formed on iron and steel at high temperatures have been shown to grow by counter-current diffusion. Oxygen

diffuses inwards and combines with the metal, while metal diffuses outwards and combines with oxygen. Thus the oxide layer thickens in both directions and the film first formed becomes an intermediate layer in the scale. It has not been shown that the oxide on other metals thickens in this way, but this is probably the general case, although in many instances the rate of diffusion of metal outwards may be almost negligible in comparison with that of oxygen inwards. The diffusion of the oxygen involves, firstly, its solution at the outer surface of the film, secondly, its diffusion through the film, and, thirdly, its combination with metal at the oxide-metal interface. The rate of oxidation of the metal therefore depends on a number of factors including the supply of oxygen to the outer surface of the film, the solubility of oxygen in it, the resistance of the film to the diffusion of oxygen, and the concentration of oxygen at the oxide-metal interface. The diffusion of metal outwards involves a similar sequence of processes and its rate depends on similar factors, viz. the solubility of metal in the oxide, the resistance of the oxide to diffusion of metal, and the rate of the reaction between the metal and oxygen at the oxide-oxygen interface. All these factors bearing on the diffusion of oxygen and metal are summed up in the term 'permeability' of the film.

It is clear that if a metal covered by an oxide film is subjected to stress this will tend to crack the film because of differences in the capacity for deformation of the two substances. The importance of this in connexion with corrosion-fatigue has already been described (Chapter VII). Furthermore, if the metal is subjected to temperature changes, cracking of the film will tend to occur in consequence of the difference in the coefficients of expansion of the two substances. Finally, release of internal stress in the metal (Chapter X) leading to changes in dimensions will tend to crack the oxide films. In addition to these external causes of cracking, however, oxide films tend to crack spontaneously when they attain a certain thickness. This occurs most readily in the films that occupy less volume than the metal from which they are formed and are therefore in a condition of tension. These crack when still very thin, and contract, leaving areas of fresh metal surface exposed to further oxidation. As this sequence of film formation, cracking and contraction, exposure of metal, and further oxidation continues while the metal is subjected to oxidizing conditions, the general result is similar to what would be obtained if the oxide layer was always discontinuous. In other words, as the surface of the metal is never completely covered by a film of appreciable thickness it is, in a sense, never completely protected from the oxidizing atmosphere, and consequently oxidation under constant conditions continues at a constant rate. When the oxide occupies more volume than the metal and is held in compression on the metal surface a much greater thickness must be reached before it cracks. Until this stage is reached the film grows by diffusion of oxygen (and of metal) through it. With a

given metal exposed to a given atmosphere at a given temperature the solubility of oxygen and of metal in the oxide remain constant while the thickness through which diffusion must take place increases. Thus the amount of oxygen reaching the oxide-metal interface and of metal reaching the oxide-oxygen interface decreases as the film becomes thicker. In other words the rate of oxidation decreases as it proceeds. It will be shown presently that when the oxide occupies less volume than the metal there is a linear relationship between the amount of oxide and time, whereas, when the oxide occupies more volume than the metal the relationship is parabolic.

It follows from the above that in the case of metals that form oxides which occupy more volume than the metal the rate of oxidation will fall off progressively until it becomes negligible or the oxide cracks. If the rate of oxidation becomes negligible before the film becomes thick enough to crack, no further oxidation will take place unless the conditions are altered. The metal is then protected by the oxide film. If, however, the oxide attains the thickness necessary for cracking before the rate of oxidation becomes negligible, then oxidation will continue more or less intermittently. When the first cracks appear the stress in the film is to some extent relieved and oxygen has free access through them to the surface of the metal exposed by the bending up of the original film near the cracks. This new oxidation at the cracks will soon seal them, but the film as a whole is not impervious to oxygen and on further thickening will again crack. Thus if a film reaches a thickness sufficient to cause cracking before it becomes impervious to oxygen, oxidation is liable to continue indefinitely in a series of steps, involving cracking followed by rapid oxidation, then oxidation at a decreasing rate until more cracks form, and so on.

The behaviour of continuous oxide films is influenced by several inter-related factors. In the first place, if the oxide is impermeable to oxygen its growth will cease while it is still very thin, whereas if it is readily permeable it will tend to continue to grow at an appreciable rate until a considerable thickness is attained. Secondly, if the oxide is brittle it will crack while still quite thin whereas if it is plastic it will respond to the imposed compressive stress by deforming. The relations between permeability and plasticity vary with the metal and the temperature. Thus the oxide film formed on aluminium at room temperature is much more impervious than that formed on copper, but it is also more brittle, and consequently, the oxidation of aluminium at room temperature is accompanied by intermittent cracking although the rate of thickening of the film is extremely slow, while that of copper proceeds without cracking although the thickening of the film is much more rapid. Furthermore, when copper is exposed to dry air at atmospheric temperature the film never becomes thick enough to crack, but if the metal is heated in air the cracking stage is reached. On further heating, however, as a result of the increased plasticity of the oxide, thickening

proceeds without cracking. Other factors that must affect the behaviour of continuous films are connected with the relative rates of diffusion of oxygen and metal. If, e.g., oxidation takes place almost entirely by inward diffusion of oxygen then all subsequent layers of oxide will be formed below the original one. As the oxide occupies more volume than the metal the formation of oxide under the original layer will expand this layer. This will in the first place relieve the compressive stress. If, however, oxidation takes place by inward diffusion of oxygen and outward diffusion of metal then subsequent layers of oxide will be formed both above and below the original one. As metal is diffusing outwards leaving space for the formation of oxide below the original layer, and as this metal is oxidized at the oxide-oxygen interface forming layers that may be held either in tension or compression, it is evident that the stress conditions in films formed by counter-current diffusion will be different from those in films formed by oxygen diffusion only. This will clearly influence the phenomenon of cracking. Finally, the behaviour of films is affected by sintering, which is a change in the structure of the film resulting in greater compactness and therefore greater resistance to diffusion.

It is evident from the foregoing considerations that one of the most important factors in the oxidation of metals is the relative volume of a metal and its oxide. If the oxide occupies less volume than the metal the oxide layer will be in effect discontinuous, and the rate of oxidation will be constant. If it occupies more volume than the metal the oxide layer will be, in general, a continuous protective film, and the rate of oxidation will diminish with time. Pilling and Bedworth (183) have calculated that discontinuous, non-protective oxide layers are to be expected on the metals lithium, sodium, potassium, magnesium, calcium, strontium, and barium. This is in accordance with the known behaviour of these metals. At high temperatures they burn in air, and at atmospheric temperature although oxidation is comparatively slow it does not tend to fall off. Vernon (184) has shown that zinc also behaves in this way at atmospheric temperature, and so, to some extent, does iron. The other common metals copper, aluminium, lead, tin, nickel, and chromium form continuous protective films, and their behaviour under oxidizing conditions depends on the permeability and plasticity of these films, the relative rates of diffusion of oxygen and metal through the films, and whether any changes resulting in sintering occur.

Ultra-thin Invisible Films.

When silver is exposed to iodine vapour at atmospheric temperature continuous iodide films are formed and grow to a considerable thickness by diffusion of iodine through them. Similarly, when copper is exposed to atmospheres containing sulphur compounds the continuous films go on thickening. At room temperature, however, continuous oxide films

are highly impervious to oxygen and thus become protective while still very thin. Such ultra-thin films are very transparent and are quite invisible while on the metal. Until recently it was largely a matter of opinion whether they existed or not, and the oxide film was simply a convenient hypothesis that enabled certain phenomena to be explained. The position is now quite different, for as a result of the careful experiments of a number of investigators their existence has been definitely proved by means of delicate weighing, changes in optical properties, and the actual separation of the film from the metal. By very accurate weighing Vernon (185) showed that when copper was exposed to pure dry air for one day, it increased in weight to the extent of 0.03 mg. per 100 sq. cm. of surface. During a further exposure of twenty-nine days no additional increase in weight occurred, and the first weight increment was evidently due to the formation of a film that protected the metal from further oxidation. Freündlich and his collaborators (186) in Berlin have perfected a delicate optical method by means of which the presence of ultra-thin films may be detected and their thickness measured. The most direct method of demonstrating their existence is, however, that which depends on removing them from the surface of the metal. This has been done for a number of metals. When aluminium is heated in a current of pure dry hydrogen-chloride, the metal is converted to chloride and distils away leaving the oxide film as a thin transparent membrane. Similarly, the oxide skin on iron may be isolated by dissolving away the metal with a concentrated solution of iodine in potassium iodide. This method has been used successfully by Evans and his collaborators. These investigators have also perfected a method of isolating oxide films by anodic treatment and have thus removed the films from copper, nickel, pure iron, mild steel, and stainless steel (see Evans (187)). After the film that is to be studied has been formed on the metal, one end of the specimen is trimmed so as to remove it and permit access of the electrolyte to the metal-oxide interface. The specimen is then made the anode in a U-shaped electrolytic cell containing a cathode. The current flowing produces dissolution of the metal of the anode, which commences at the bottom where the film has been cut through by the trimming. The attack extends upwards just below the film, since the portion of metal just below the film is specially susceptible to attack as a result of the original abrasion of the surface. Thus the film is undermined and loosened and finally peels off in curling flakes.

Up to a thickness of 200 Å. ($1 \text{ Å.} = 10^{-8} \text{ cm.}$) oxide films remain invisible when attached to the surface of a metal but become visible by transmitted light when they are isolated. Above 400 Å. they become visible by interference while on the metal, as will be explained presently. Owing to the slow rate of diffusion through continuous oxide films at atmospheric temperature a very thin layer of oxide is sufficient to retard further oxidation. If the surfaces of metals were absolutely smooth

and free from such irregularities as cracks and pores, a quantity of oxide sufficient to provide a layer one molecule thick should afford some protection. Actually, however, the surface of a metal, particularly after abrasion, is shattered on a minute scale, and oxide forms in the crevices and pores before a continuous coating is produced. The optical research carried out in Freündlich's laboratory indicates that the oxide films formed on iron mirrors (produced on glass by heating iron carbonyl vapour) by the action of air are about 10 Å. thick, and Vernon (184) likewise found by his gravimetric method that the thickness of the film required to protect copper was about 10 Å. These dimensions are of the same order of magnitude as the molecules of the oxides, and it appears that under certain conditions protection may be afforded by such films. Usually, however, owing to the shattered nature of the surface the oxide films are about 20 times as thick.

In order to facilitate the removal of the oxide layers the surface of the metal is abraded before being oxidized. As oxide is formed in the cracks and pores produced by abrasion the first stage in oxidation results in the formation of a layer of interlocked metal and oxide. When very thin films are isolated from the metal they are therefore found to contain numerous particles of it. If further oxidation is promoted by heating the metal in air, or by other means, the shattered layer of metal is ultimately converted completely to oxide, and when the film is isolated a clean separation of oxide and metal is obtained. As, however, metal that has not been abraded also contains crevices and pores which are smaller and less frequent than those in abraded metal, there is always some penetration of oxide into the metal below the surface film, and the surface of a metal from which a film has been removed is different from a fresh surface.

The films produced on metal by exposure to air under conditions that do not permit the condensation of moisture on its surface protect the metal against further oxidation under these conditions. In general, also, any conditions that result in the formation of thin continuous films will result in the metal becoming protected against these conditions. To a certain extent, however, the films formed under one set of conditions may also protect the metals either wholly or partly against attack under other conditions. Thus, highly protective films are formed on the metals aluminium, chromium, and nickel by exposure to air or other oxidizing conditions, and these protect the metals against corrosion under a variety of circumstances so long as oxygen is present to heal any cracks that may form. The other common metals do not develop such highly protective skins, but these may usually be improved by immersing the metals in oxidizing solutions. One of the best-known examples of this is the effect on iron of concentrated nitric acid. When immersed in this, iron is unattacked, although dilute nitric acid dissolves it readily. The reason is that concentrated nitric acid is an oxidizing agent and immersion in it causes a protective oxide film to be

formed on the metal. On removal from the acid the iron displays an enhanced resistance to attack by other reagents. Similar effects are produced by immersion in solutions of oxidizing agents such as potassium chromate or in fairly concentrated solutions of alkaline salts.

Interference-colour Films.

Thin films on metals are transparent. Light striking a specimen is mainly reflected through the film from the surface of the underlying metal, but some is also reflected from the surface of the film. When they are very thin the films are invisible on the metal, but when they reach a certain thickness they give rise to interference colours and their presence is revealed.

Ordinary white light consists of rays extending over a wide range of wave-lengths, and at certain film thicknesses rays of a given wave-length reflected from the surface of the film are out of phase with those reflected from the surface of the metal. When this condition is realized those particular rays are extinguished, the reflected light does not contain this colour, and the surface of the specimen therefore displays the complementary colour. As the thickness of the film increases, the first rays to be extinguished are those of the shortest wave-length, i.e. the blue rays. When the film attains a thickness equal to one-quarter the wave-length of blue light the reflections of this from the film and metal respectively are out of phase. There is no blue in the light reflected from the specimen and it therefore displays a yellow colour. With further increase of thickness the green rays are next extinguished, and the surface reflects a reddish tint. At a still greater thickness interference of the yellow waves occurs and the specimen assumes a blue colour; next the red waves are extinguished and a greenish tint is produced; and finally when the wave-lengths cut out are too long to affect the eye the original colour of the metal appears. As the film continues to thicken, however, the sequence of colours is repeated, since interference of light of a given wave-length occurs not only when the reflections differ by $\frac{1}{4}$ of a wave-length, but also when they differ by $\frac{3}{4}$, $1\frac{1}{4}$, or $1\frac{3}{4}$ wave-lengths. It might be expected that in this way the whole sequence of colours would be repeated many times, but owing to the fact that various orders of reflections tend to overlap there is a certain modification of the sequence. Furthermore, on certain strongly coloured metals like copper, the colour of the metal modifies the effect of interference, and on all metals the film becomes more and more opaque as its thickness increases so that a stage is reached at which no light is reflected from the metal, and the film displays its natural colour. At this stage the oxide layer has ceased to be a film and is more properly described as a 'scale'.

The oxide films formed on metals by exposure to comparatively pure air at atmospheric temperature do not become thick enough to display interference colours. These films become impermeable to oxygen

while they are still invisible. If the temperature is raised, however, diffusion of oxygen through the film is facilitated, and by controlling the time and temperature of exposure any desired oxide tint may be produced. By changing the conditions under which the metal is exposed interference colours may also be produced at ordinary temperature. Thus silver exposed to iodine vapour at ordinary temperature gives a wonderful sequence of tints due to iodide films, and copper exposed to air containing hydrogen sulphide or hydrogen chloride shows the same series of colours as are obtained by heating.

Silver iodide is a transparent substance and for this reason iodide films on silver show several orders of interference colours as follows: 1st Order: Yellow or Brown, Red Mauve, Blue Mauve, Blue, Silvery or Green; 2nd Order: Yellow, Red, Blue, Green; 3rd Order: Yellow, Red, Green; 4th Order: Red, Green; 5th Order: Red (Evans (187)). Exactly the same sequence is shown by the oxide colours produced on molten lead when exposed to air. Both the silver-iodide film and the lead-oxide film can be transferred from the metal on to glass or mica, and in both cases the films themselves show colours when on the transparent base. When the film-substance is less transparent the later colours are absent. Thus in the oxide colours on copper or nickel it is difficult to distinguish clearly anything beyond the third order, and on iron, where the oxide film is still less transparent, only the first-order tints are conspicuous. By progressively reducing the thickness of interference-colour films the colours may be obtained in the reverse order. This has been accomplished on iron by three different methods. Mason (188) reduced the thickness of the film by the action of very dilute nitric acid, Gale (189) by careful polishing, and Evans (190) by cathodic treatment in very dilute hydrochloric acid. Constable (191) has measured the actual thickness of the film producing different colours on iron.

The thickness of the oxide films produced on metals by heating depends both on time and temperature, but, as is the case with numerous other phenomena, a small rise in temperature has the same effect as a large increase in time, and consequently for moderate periods of exposure the interference colour is an approximate indication of the temperature. They have long been used for this purpose in the operation of tempering, i.e. decreasing the hardness of quenched steel by reheating. As this process also depends on time and temperature, heating the metal until a certain temper colour is developed is a fairly reliable guide. The following tables due to Brearley (192) show (1) the approximate temper colours corresponding to various temperatures in the range used for tempering tools, and (2) the effect of time at certain temperatures on the colour produced.

As the tendency to crack increases with the thickness of the film, interference-colour films are more liable to be cracked than thinner invisible films, and in consequence they are frequently less protective. The metals that are most resistant to oxidation at elevated temperatures

are therefore those that form films which become impervious to oxygen while still very thin viz. aluminium, nickel, and chromium. Heating metals in order to produce oxide films is, in certain cases, a convenient way of protecting them against corrosion at atmospheric temperature, but the protection afforded by the treatment is not always reliable owing to the fact that corrosion proceeds easily once the skin is broken. Again, the best protection is provided by films which are formed under the service conditions for these are then 'self-healing'. Vernon (184) has shown, however, that heating copper or brass at temperatures as low as 75° C. results in a pronounced increase in their resistance to

TABLE 43 (a)

<i>Colours</i>					<i>Temperatures</i>
Light straw	225° C.
Dark straw	240° C.
Yellow brown	255° C.
Red brown	265° C.
Purple	275° C.
Violet	285° C.
Cornflower blue	295° C.
Pale blue	310° C.
Sea green (or grey)	330° C.

TABLE 43 (b)

<i>Temperature</i>	<i>Straw</i>	<i>Brown</i>	<i>Purple</i>	<i>Dark blue</i>	<i>Pale blue</i>
200° C.	6 min.	49 min.
220° C.	3 "	33 "	63 min.
250° C.	1 "	10 "	39 "
275° C.	0.5 "	3 "	11 "	27 min.	40 min.

atmospheric tarnishing, and treating iron or steel so as to produce a blue oxide coating is one of the recognized methods of preserving these metals. Such thick oxide coatings provide a certain amount of protection against atmospheric corrosion, but it appears that thinner films are actually more protective. When drops of dilute copper-nitrate solution are placed on freshly cleaned iron the iron replaces copper in solution, and copper is deposited immediately. If the iron is exposed to the air for some time before the copper nitrate is applied a slightly longer time elapses before copper is deposited. But as the oxide film that is formed on iron at ordinary temperatures is not continuous except when extremely thin, the protection afforded is not conspicuous. If an iron strip is heated at one end only, a visible oxide scale forms at the heated end. Proceeding towards the cold end the coating becomes progressively thinner and passes through the range of interference colours before becoming too thin to be visible. When drops of copper nitrate are placed at intervals along the strip it is found that metallic copper is immediately deposited at the end which has not been heated,

but farther along the strip, before the temper colours are reached, the deposit becomes less and less, and finally ceases. When the temper colours are reached, however, deposition is again observed at scattered points which are cracks in the film, thus demonstrating that as a result of their less perfect continuity thick films are less protective than thin ones.

Atmospheric Oxidation at Ordinary Temperature.

At elevated temperatures the action of the atmosphere on metals is one of direct oxidation which is almost entirely controlled by the composition of the metal, the time, the temperature, the oxygen pressure, the nature of the oxide layer, and the chemical or physical changes in this layer. The phenomenon is also influenced by the presence of such gases as water vapour, sulphur dioxide, and chlorine compounds; but these have not such a pronounced effect on high temperature oxidation as atmospheric impurities and moisture have on corrosion at ordinary temperature. At this temperature small amounts of sulphur dioxide, hydrogen sulphide, hydrogen chloride, carbon dioxide, and ammonia present in the atmosphere frequently exercise a controlling influence, and the progress of corrosion also depends to a great extent on whether or not water deposits on the surface of the metal. As water may be deposited directly as rain, condensed from the atmosphere, absorbed by a deliquescent corrosion product or by deliquescent particles deposited from the atmosphere, direct oxidation at ordinary temperature is frequently associated with electrochemical corrosion. In many respects, however, the behaviour of metals when exposed to the atmosphere at ordinary temperature is a typical example of direct oxidation, and for this reason some features of this behaviour may be described in order to give concrete illustrations of direct oxidation and its relation to other phenomena.

Pure dry air consists of nitrogen, oxygen, and argon in the respective proportions by volume of 78.06, 21.00, and 0.94 per cent. Of these gases oxygen is the only one that reacts with metals. Consequently, in pure air direct oxidation is the only change that can take place. The ordinary atmosphere is not, however, pure dry air. At any given temperature, air at normal pressure may absorb a certain quantity of water vapour. When it contains this quantity it is said to be saturated at that temperature, and if the temperature falls water will be deposited as moisture. Saturation of air can only occur, however, when water is available, and the moisture content of unsaturated air is most conveniently expressed as the relative humidity, i.e. the amount of water vapour actually present stated as a percentage of that required for saturation. If the relative humidity of the air is less than 100 per cent. it may be cooled without immediate deposition of water, but as its capacity for retaining moisture decreases with the temperature, it will ultimately become saturated and deposit moisture if cooled to a sufficiently low

temperature. For air with a given content of water vapour there is a particular temperature at which it precipitates water when cooled. This is called the dew-point. Above the dew-point moisture will not condense on the exposed surfaces of metals, but when the temperature falls below the dew-point, water is deposited and probably remains in minute pores and crevices on the surface of the metal after the temperature of the air has risen again.

If the surface of a metal exposed to the atmosphere is in contact with any hygroscopic substance (i.e. a substance that absorbs moisture from the atmosphere even when it is unsaturated) water collects on the surface of the metal even above the dew-point. As the products of corrosion are frequently hygroscopic a surface on which corrosion has started may remain wet although no direct condensation is taking place. The absorption of moisture by hygroscopic substances varies considerably with the humidity of the atmosphere, and in many cases there is a 'critical humidity' below which absorption is small and above which it is large. Under the appropriate circumstances this 'critical humidity' has an important influence on corrosion. In the absence of a deliquescent corrosion product the same effects may be obtained by the deposition of deliquescent particles from the atmosphere.

Water and air are capable of producing a sensible amount of rusting on iron and steel, but in the absence of polluting agents the action is extremely slow even where the precipitation of moisture is considerable. In inland regions the chief sources of impurities that promote corrosion are the numerous coal-fires used industrially and domestically and the discharge of gases from chemical works. From these, quantities of sulphur compounds are added to the atmosphere and exercise an important influence on corrosion, particularly in large towns and industrial areas. Near the sea the atmosphere contains a certain amount of salt spray, and even in inland atmospheres chlorides are present. From the point of view of pollution five general types of atmosphere may be distinguished; urban, industrial, suburban, marine, and rural, and three different kinds of exposure to each atmosphere may be recognized, indoors, outdoors but protected from rain, and outdoors unprotected from rain. The progress of corrosion depends on the exact conditions of exposure, and as temperature, humidity, and content of impurities vary with the time of year this has also to be taken into account.

Copper

Several very comprehensive investigations of the effect of the atmosphere on various metals have been carried out by Vernon, and some of his work may be described in order to illustrate this phenomenon. In one experiment (185) a copper specimen was exposed to pure dry air for a period of 40 days. No visible change took place, but the formation of oxide was detected by accurate weighing. As previously stated during the first day the specimen increased in weight by an amount

equal to 0.03 mg. per 100 sq. cm. of surface area. Thereafter no further increase in weight occurred. A specimen similarly exposed to pure air saturated with water vapour (relative humidity 100 per cent.) also showed no visible change after 40 days, but the gravimetric method showed that it had increased in weight by about 0.09 mg. per 100 sq. cm. of surface area. When sulphur dioxide in concentrations varying from 0.1 to 10 per cent. was added to dry air it produced no change in the rate of oxidation. The weight increment was the same as for pure air. It follows from this that pure dry air, pure saturated air, and dry air containing sulphur dioxide have little effect on copper. In the early stages of exposure an oxide film is formed and it prevents further attack. When both sulphur dioxide and water vapour were added to the air more pronounced corrosion occurred, but as this did not result in the continuous increase in thickness of a film its consideration may be postponed until later.

Vernon (184) also carried out experiments in which specimens of several metals were exposed to the ordinary atmosphere in the basement of the Royal School of Mines. Investigation of this atmosphere showed that the sulphur content varied considerably with the time of the year. In the summer months, in the absence of domestic fires, the sulphur content was very low, and for most of the time between May and October it was less than one volume of hydrogen sulphide in 600 million volumes of air. From October until the end of December the sulphur content increased rapidly and reached a maximum of 16 volumes of hydrogen sulphide in 600 million volumes of air. Thereafter it decreased gradually until the beginning of May. A series of experiments with copper specimens exposed for stated periods at different times of the year showed that the square of the weight increment was proportional to the reactive sulphur content of the atmosphere.

From the point of view of the experiments now to be described the year may be divided into two periods—summer when the sulphur content was almost negligible, and winter when it was relatively high. Fig. 201 (lower curve) shows the increase in weight with time of a specimen first exposed in the winter period. The experiment extended over 1,300 days, and the winter and summer periods are indicated by the vertical lines. It will be noted that there is no change in the rate of attack in passing through the different periods. Fig. 202 (*A*) shows the increase in weight with time of a specimen first exposed in the summer period. The vertical line marks the beginning of the winter period, and again it will be observed that there is no change in the rate of attack on passing from one period to another. Curve *B* in Fig. 202 is the early part of Fig. 201 plotted on the same scale as Curve *A* (Fig. 202) and in its correct chronological position. The different slopes of these curves (*A* and *B*, Fig. 202) illustrate the different rate of attack on specimens first exposed in the summer and winter periods respectively.

It follows from the above experiments that the progress of subse-

quent corrosion is controlled by the conditions under which the metal is first exposed and that later changes in these conditions have no effect. After 90 days' exposure beginning in the summer and extending into the winter the increase in weight was 0.35 mg. per 100 sq. cm. of surface area, whereas after 90 days' exposure beginning in the winter and extending into the summer it was 2.0 mg. per 100 sq. cm. From this it may be inferred that the film which develops on copper at ordinary temperature in an atmosphere of relatively high purity is quite different in

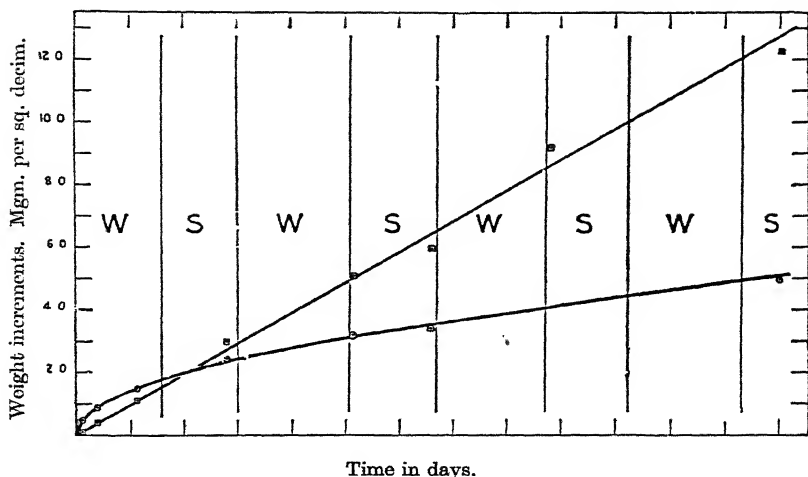


FIG. 201. Oxidation (tarnishing) of copper at ordinary temperature in atmosphere periodically contaminated with traces of sulphur compounds. Relation between weight increment and time up to 1,300 days' exposure.

□ = Squares of observed weight increments ($\times 0.5$).

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properties from that which forms in the presence of traces of sulphur compounds. In the former case the film is almost pure oxide and is relatively impermeable to both oxygen and sulphur. In the latter case some sulphur atoms are incorporated in the first-formed film which remains more permeable to both oxygen and sulphur. Once formed, this second type of film goes on thickening at the same rate even when sulphur is not present in the atmosphere, and similarly the rate of thickening of the first type is not increased by the presence of sulphur.

The upper curve in Fig. 201 represents the squares of the weight increment in curve *A* plotted against time. The broken line in Fig. 202 is also derived from the squares of the weight increments in curve *A*. As both of these are straight lines it follows that the time-weight increment curves are parabolic. The course of film formation on these specimens may therefore be represented by the equation

$$W^2 = Kt,$$

where W is the increase in weight, t the time, and K a constant. This

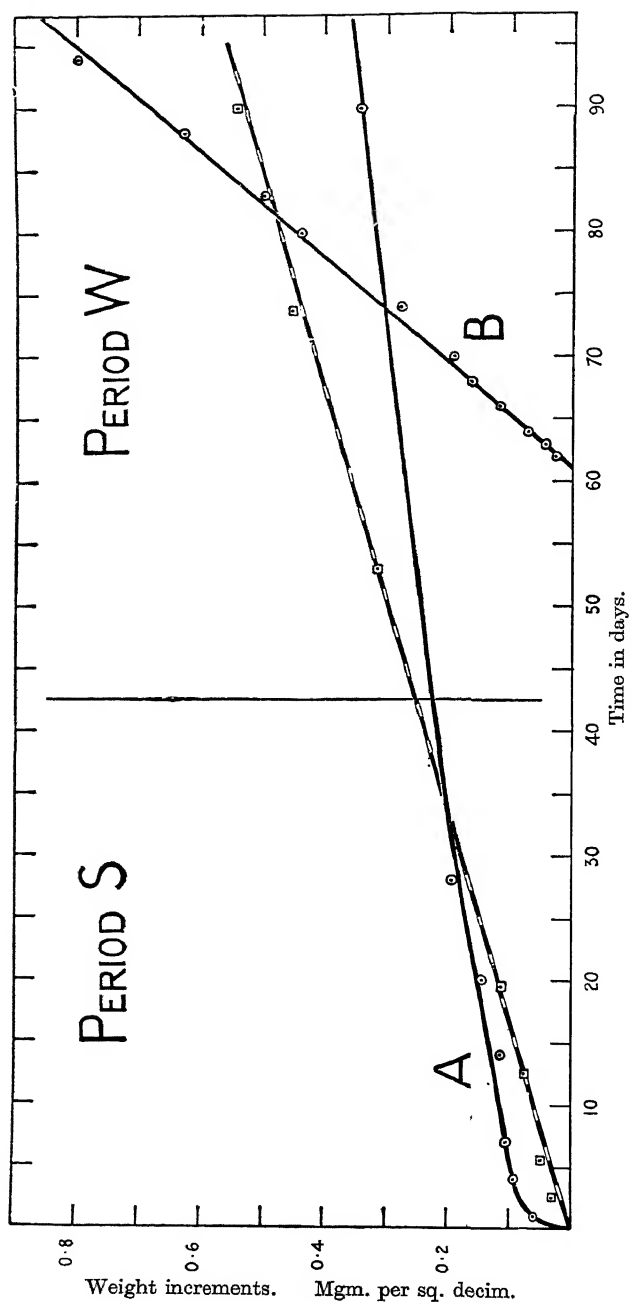


FIG. 202. **Period S** (Curve *A*).—Oxidation of copper at ordinary temperature in relatively pure atmosphere. Relation between weight-increment and time.

□ = Squares of weight increments (values taken from smooth curve) $\times 5.0$.

Period W.—Attack upon freshly-cleaned copper (Curve *B*). Immunity of copper protected by thin film of oxide. (Continuation of Curve *A*.)

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law could be deduced on the assumption that oxidation is controlled by the diffusion of oxygen through a protective film, and when a process of corrosion obeys such a law it indicates film formation. It has received ample experimental verification. Tammann (193) has shown that it applies to the growth of iodide films on silver, Pilling and Bedworth (183) have demonstrated that it also applies to the oxidation of copper, nickel, and iron at elevated temperatures, and Dunn (194) has shown that it applies to the oxidation of copper in the range of temperature just above 200°C.

With pure metals departures from the parabolic law occur if the oxide film sinters, and with alloys departures occur due to other changes in the oxide film or the underlying metal surface. Moreover, a number of investigators have shown that in the early stages of oxidation when the film is very thin, and at all stages when the oxygen pressure is low, the law is not obeyed. Evans (195) points out that the law will be obeyed when the oxygen pressure is high enough to keep the outer surface of the oxide saturated, and when the film is thick enough to transmit oxygen so slowly that it is taken up by the metal as quickly as it arrives at the oxide-metal interface. Hence the parabolic law may be expected to hold good for fairly high pressures and fairly thick films but not for very low pressures and very thin films. This is found to be the case, and in the early stages of oxidation the oxidation-time curve is a straight line rather than a parabola. In general, therefore, the equation connecting time and amount of oxidation has the form

$$W^2 = Kt + C,$$

and the value of C is not zero as supposed in the Tammann-Pilling-Bedworth law.

The protective character of the film obtained by exposing copper to a relatively pure atmosphere suggested to Vernon that a similar degree of protection might be conferred more rapidly by exposure to a higher temperature. Preliminary experiments showed that the formation of a protective film by heating was independent of the prevailing atmosphere and that no purification was necessary. Specimens were then heated for one hour at 50°, 75°, 100°, 125°, 150°, 175°, 200°, 225°, 250°C. respectively, and exposed to the atmosphere at ordinary temperature along with an untreated specimen. After 20 days the untreated specimen and that heated at 50°C had tarnished to a reddish-purple colour, but no change had taken place on any of the specimens heated at 75°C. and higher. Weight-increment experiments showed that the rate of oxidation on exposure to the atmosphere after heating decreased rapidly as the heating temperature was raised from 50° to 75°C. and then more slowly.

In view of the characteristic properties of oxide and oxy-sulphide films disclosed by the above experiments there is considerable interest in the behaviour of pure sulphide films. Two specimens of copper were heated in air at 150°C. for 20 minutes and 1 hour respectively in order

to produce (*A*) an orange interference film approximately 150 Å. thick and (*B*) a rose interference film approximately 300 Å. thick. Two other specimens were exposed to hydrogen sulphide at atmospheric temperature until films corresponding in thickness to (*A*) and (*B*) were produced. The four were then subjected to the atmosphere in the winter period together with two freshly abraded and untreated specimens. In striking contrast to the heat-treated specimens which showed no signs of change even in 12 months, those initially covered with sulphide proceeded at a modified rate through the same succession of colour changes as they would have done if the treatment with hydrogen sulphide had been continued. Their rate of change was visibly greater than that of those exposed in the freshly cleaned condition. After one month's exposure the specimens were weighed and the sulphur content of the films determined. The results are shown in the following table:

<i>Initial film</i>	<i>Weight increment during one month's exposure to atmosphere</i>	<i>Proportion of weight increment due to sulphur</i>
Thin oxide . . .	0.25 mg. per 100 sq. cm.	1.0 per cent.
Thick „ . . .	0.18 „ „ „	
Thin sulphide . . .	1.64 „ „ „	26.2 per cent.
Thick „ . . .	1.71 „ „ „	
Freshly cleaned . . .	1.10 „ „ „	14.8 per cent.

From these results it will be seen that the presence of the initial sulphide film has not only caused a definitely greater attack on the underlying metal but has also increased the selective absorption of sulphur from the atmosphere. On the other hand the protective influence of the initial oxide film is demonstrated by the fact that sulphur is virtually unable to penetrate it.

From the foregoing experiments on copper it may be concluded that films of pure oxide are relatively impervious to oxygen atoms and impervious to sulphur atoms. Pure sulphide films on the contrary are relatively pervious to both oxygen and sulphur atoms, and moreover they favour the selective absorption of sulphur. Exposed to the ordinary atmosphere containing traces of sulphur as impurity, sulphide films increase in thickness mainly through absorption of oxygen, and probably oxide-sulphide solid solutions are produced. In the case of a clean copper specimen exposed to a similar atmosphere solid solution-films are produced at the outset. These films contain a preponderance of oxide over sulphide, but the permeability is much greater than that of the pure oxide and is not very different from that of the pure sulphide.

Exposure of copper to synthetic atmospheres made by adding water vapour and sulphur dioxide to pure air did not result in the formation of films. Reference has already been made to Vernon's experiments with synthetic atmospheres, and some of his results are shown in Fig. 203. Curve *A* is the oxidation time-curve for pure dry air and also for dry air containing varying quantities of sulphur dioxide.

Curve *B* is the oxidation time-curve for pure saturated air. None of these atmospheres produce appreciable oxidation, but when sulphur dioxide and water vapour are present together the rate of oxidation increases with increase in the content of sulphur dioxide and with increase in the relative humidity. Curves *C* to *H* in Fig. 203 show the

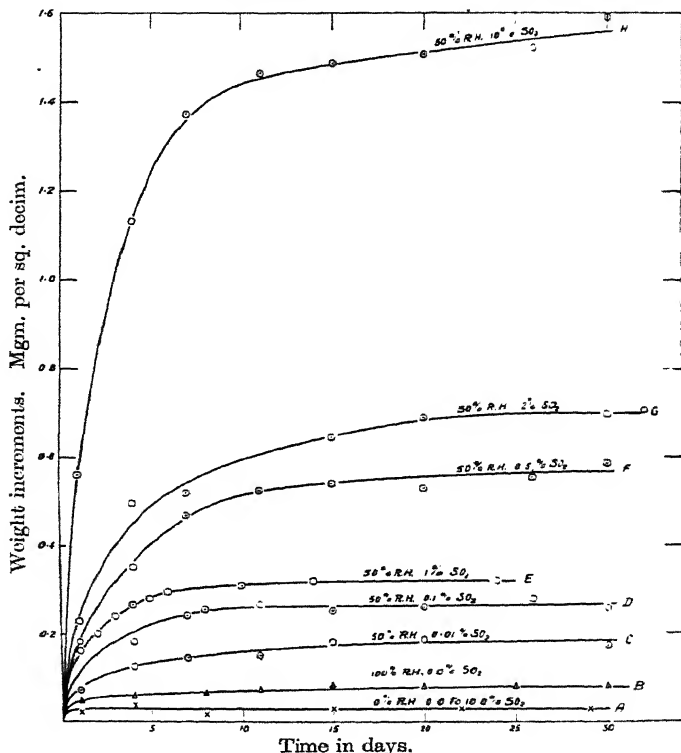


FIG. 203. Curve *A*. Atmospheres of zero relative humidity (0.0 to 10.0 per cent. SO_2).

Curve *B*. Atmosphere of 100 per cent. relative humidity (0.0 per cent. SO_2).

Curves *C* to *H*. Atmospheres of 50 per cent. relative humidity (0.01 to 10.0 per cent. SO_2).

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effects of 0.01, 0.1, 0.5, 1.0, 2.0, and 10.0 per cent. of sulphur dioxide in atmospheres of 50 per cent. relative humidity. These curves are all similar in form, but they are not parabolic, and this indicates that the mechanism in this case does not depend on diffusion through a continuous film. They are exponential at first, and then tend to flatten out and become parallel to the time axis. The exponential portion persists for a longer time the higher the concentration of sulphur dioxide, but the approximate equilibrium value, represented by the nearly horizontal portion of the curve is reached in all cases after about 30 days' exposure.

The total effect of atmospheres of 50 per cent. relative humidity containing varying concentrations of sulphur dioxide was very small, and none of the specimens showed more than a slight darkening after 30 days' exposure. Increasing the relative humidity to 63 per cent. did not have much effect on the rate of attack, but a further increase to 75 per cent. resulted in a pronounced acceleration of oxidation. The results obtained for atmospheres of 75 and 99 per cent. relative humidity containing varying concentrations of sulphur dioxide were of quite a different order from those shown in Fig. 203. This may be illustrated by comparing the increase in weight after 30 days of specimens exposed to atmospheres containing 10 per cent. of sulphur dioxide but of different relative humidities. Thus in atmospheres of 50, 63, 75, and 99 per cent. relative humidities the weight increases were respectively 1.6, 2.0, 80, and 88 mg. per 100 sq. cm. These results clearly point to the existence of a 'critical humidity' between 63 and 75 per cent. relative humidity. Below the critical value the moisture content of the atmosphere has a relatively small effect, above it a pronounced one.

Reference to Fig. 203 shows that the oxidation curve for the atmosphere containing 1 per cent. of sulphur dioxide lies below that for the atmosphere containing 0.5 per cent. Similar results were obtained in all the experiments with atmospheres of different relative humidity. When the total weight-increment after 30 days' exposure was plotted against the content of sulphur dioxide a definite minimum occurred on all curves at about 1 per cent. of sulphur dioxide. This shows that this value is a 'critical concentration' of sulphur dioxide.

When a small amount of hydrogen chloride (0.01 per cent.) was added to an atmosphere containing 1.0 per cent. of sulphur dioxide the rate of oxidation was greatly increased, a parabolic oxidation-time curve was obtained, and interference colours were produced. In this case, therefore, film formation took place, but in the experiments with atmospheres consisting only of air, water vapour, and sulphur dioxide the oxidation-time curves were not parabolic and no interference colours were produced. It may therefore be concluded that in such atmospheres oxidation does not involve film formation. Vernon came to the view that under those conditions the process is controlled by the catalytic oxidation of sulphur dioxide to sulphuric acid at the metal surface, the rate of attack falling off as the active centres are used up. Thus the oxidation-time curves show that the attack decreases with time but not in the same way as when film formation occurs.

On the basis of the catalytic hypothesis Vernon was able to explain the effect of 'critical concentration' and 'critical humidity'. Analysis of the corrosion products formed in different atmospheres showed that in those containing less than 1 per cent. of sulphur dioxide the product consisted of copper sulphate and copper hydroxide, in those containing 1 per cent. of sulphur dioxide it was composed of copper sulphate only, whilst in those containing more than 1 per cent. of this gas, copper

sulphate in the product was accompanied by excess sulphuric acid. Thus the 'critical concentration' of sulphur dioxide is that required to form a corrosion product consisting entirely of copper sulphate. The 'critical humidity' was found to depend on the hygroscopicity of the corrosion product which underwent a marked increase between 50 and 75 per cent. relative humidity.

In all cases in which metals are exposed to the atmosphere while screened from rain, the hygroscopicity of the corrosion product is important. Under such conditions the corrosion product remains in contact with the metal, and the atmospheric humidity at which condensation takes place depends on the hygroscopicity of this product. According to Hudson (196) there is probably a critical humidity for each corrosion product above which condensation occurs. The metals yielding the corrosion products with the lowest critical humidities are liable to be the most corrodible under these conditions of exposure since, when condensation does occur, the metal is in contact with a well-aerated solution of its corrosion product and the conditions are ideal for intense electrochemical corrosion. Laboratory tests carried out by him on the deliquescence of a number of corrosion products revealed that the amount of corrosion suffered by metals exposed to the atmosphere but protected from rain was related to the deliquescence of their corrosion product. Thus copper, copper-cadmium, phosphor-bronze, and aluminium gave rise to corrosion products that were not markedly deliquescent, and these metals suffered much less corrosion than nickel, copper-nickel, nickel-silver, and brass, which gave rise to deliquescent corrosion products. Experiments designed to determine the critical humidity showed that for brass, nickel, copper-nickel, and zinc there was a marked increase in the amount of moisture absorbed by their corrosion products at relative humidities between 70 and 85 per cent.

The results obtained in these experiments on the effect of deliquescent-corrosion products are in close agreement with the work of Vernon (197) on the 'fogging' of nickel. On account of the readiness with which protective films are formed on this metal it is widely used in the pure state or as a constituent of alloys when resistance to corrosion or high temperature oxidation is required. For this reason, and also because of its brilliant lustre and high degree of whiteness, it is used extensively as a protective and decorative coating. In an indoor atmosphere, maintained sufficiently above the dew-point, a polished nickel surface remains bright apparently indefinitely. If, however, the minimum temperature approaches the dew-point a dull creamy film is formed on the surface. Vernon succeeded in producing this film in synthetic atmospheres. As long as the content of sulphur dioxide did not exceed 0.003 per cent., specimens remained bright in an atmosphere of 50 per cent. relative humidity, but when the humidity was increased to 75 per cent., fogging was produced in one day. This confirmed previous observations that fogging was largely controlled by humidity and did

not occur unless this exceeded 70 per cent. As a result of his experiments Vernon concluded that the mechanism of fogging was similar to the corrosion of copper in highly humid atmospheres containing sulphur dioxide, viz. catalytic oxidation of sulphur dioxide to sulphuric acid and the formation of sulphate. It was found that prolonged exposure to stagnant air at ordinary temperature induced a large measure of immunity to fogging on subsequent exposure. A similar effect could not be produced by short periods of exposure at higher temperatures. It was concluded therefore that immunity was not obtained by film formation but by poisoning (i.e. destruction of the catalytic activity) of the surface by small traces of an anti-catalyst.

Zinc.

Using the gravimetric method Vernon (184) studied the behaviour of zinc when exposed to the atmosphere and found that from the first day onwards throughout a period of 1,300 days the increase in weight was a linear function of time. At the end of the exposure the zinc had increased in weight by an amount equal to 20.8 mg. per 100 sq. cm., whereas the increase in weight of copper specimens exposed simultaneously was only 5.4 mg. per 100 sq. cm. Despite the large increase in weight no interference colours were shown by the zinc during oxidation.

The linear form of the weight increment-time curve for zinc and the absence of interference colours suggested that the process of oxidation does not involve diffusion through a film, and indicates that in this case a porous oxide is formed which does not tend to protect the underlying metal. These inferences were confirmed by microscopic examination, and at a magnification of 150 diameters the discontinuous granular nature of the oxide could be seen. Although such a coating is incapable of producing interference colours which depend on the thickness of a transparent film it can give rise to diffraction colours which depend on the spacing of the particles. Thus Vernon found that after a sufficiently long exposure zinc developed a blue tint which did not subsequently change with time. As the increase in weight followed a straight line for a period of three and a half years it is evident that the corrosion of zinc is not affected by seasonal variations in atmospheric conditions within the limits realized in the basement of the Royal School of Mines. In the case of copper, insusceptibility to seasonal variations is accounted for by the fact that the film first formed controls the subsequent rate of attack. This explanation is not applicable to zinc, and it must therefore be inferred that the corrosion of this metal is not affected by changes in relative humidity and reactive sulphur content within certain limits.

Brass.

The weight increment-time curves for two different brasses during an exposure of 1,660 days are shown in Fig. 204 (lower portion), along with a curve for copper simultaneously exposed. When the squares

of the weight increments are plotted against time (upper portion) it is revealed that the attack on the brasses follows the parabolic law up to an exposure of 400 days in the case of the 60:40 brass and 550 days in the case of the 70:30 brass, but that thereafter the rate of attack is a linear function of time. It follows therefore that the oxidation of these copper-zinc alloys obeys the same law as copper during the early stages

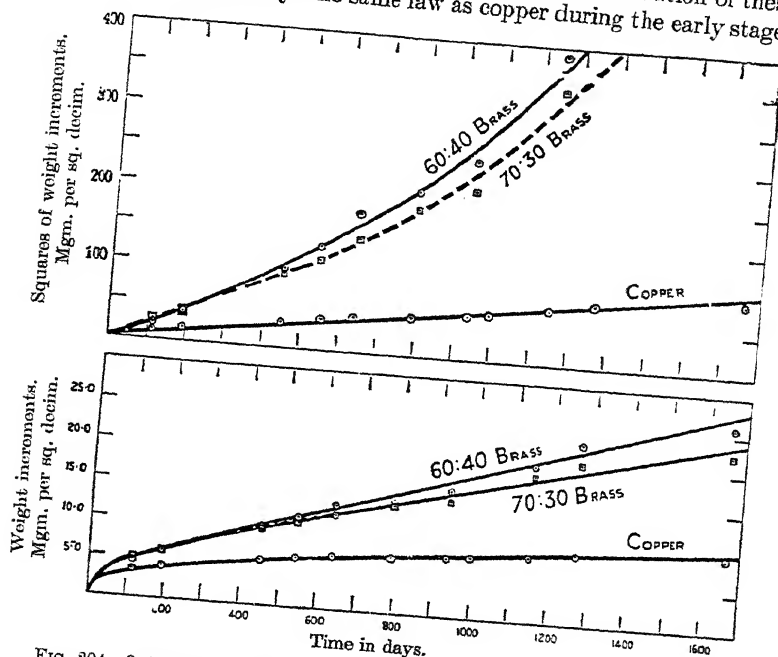


FIG. 204. Oxidation (tarnishing) of copper, 70:30 and 60:40 brass. Atmosphere type 1. 'Long Period.' Relation between weight increment and time.

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and the same law as zinc during the later stages. In the 60:40 brass the change from the parabolic to the linear relationship was shown by microscopic examination to be accompanied by a change in the distribution of attack. This alloy consists of two constituents α and β , of which the former contains a higher proportion of copper and therefore a lower proportion of zinc than the latter. Microscopic examination of this alloy at various stages of exposure showed that the attack was at first confined to the α -constituent which developed an apparently continuous tarnish film in the same way as copper. Later, however, a change of quite a different kind took place on the β -constituent and led to the production of a discontinuous corrosion product. The beginning of this type of attack coincided with the change from the parabolic to the linear oxidation-time relationship.

Besides being exposed to the basement atmosphere already described,

specimens of the metals studied by Vernon were also exposed in a tank room where the humidity was higher and the mean temperature lower. The oxidation of copper and zinc in this atmosphere was slower than in the basement because of the lower temperature, but the characteristic types of oxidation-time curves were still adhered to. There was, however, a radical change in the behaviour of brass when exposed in the tank room. In the early stages the rate of attack was a linear

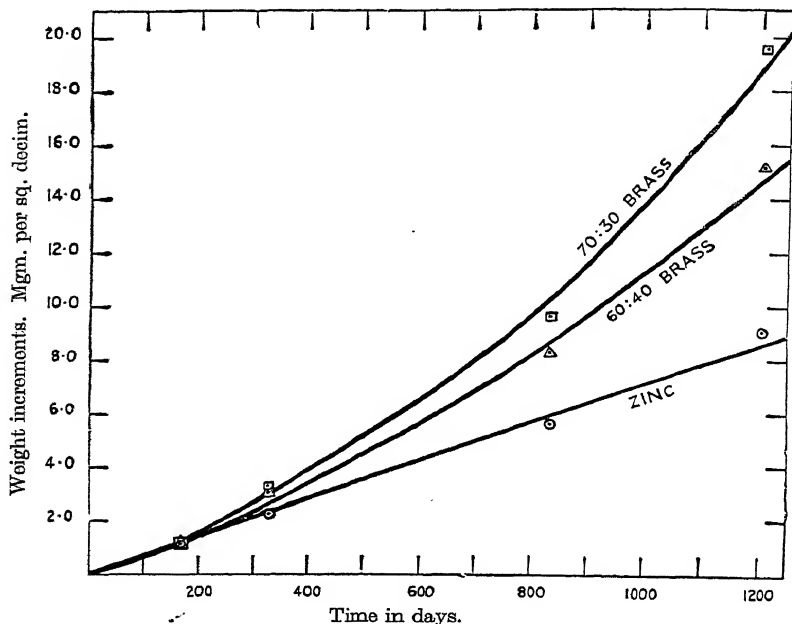


FIG. 205. Relative behaviour of 70:30 and 60:40 brass and zinc in atmosphere type 2. ('Tank-room').

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function of time, but as it proceeded it became more rapid as shown in Fig. 205 where the weight increments of the brasses are compared with zinc. The reason for this appears to lie in the nature of the corrosion product which in the case of brass was evidently capable of absorbing moisture from the more humid atmosphere of the tank room.

Another respect in which the behaviour of brass was found to differ from that of copper or zinc was in the effect of seasonal variations in the atmosphere. In the case of these metals there was no change in the rate of attack on passing from the summer to the winter period, but brass specimens exposed for three months in the summer period displayed a pronounced increase in the rate of attack on passing into the winter period. By heating to suitable temperatures before exposure the resistance of brass to atmospheric action was found to be increased, but the films produced in this way were not so protective as those

similarly produced on copper. In order to develop films of equivalent thickness brass had to be heated to higher temperatures than copper, and one hour at 200°C. had the same effect on it as one hour at 100°C. had on copper. The highest degree of protection was afforded by the film produced at 100°C. , and as the temperature of the preliminary treatment was raised above this it became progressively less protective. Films produced at temperatures above 350°C. did not appreciably reduce the rate of oxidation at atmospheric temperature. This is a good example of their tendency to become less continuous and consequently less protective as their thickness increases.

Aluminium and Lead.

Aluminium is notable for the impervious character of the oxide film developed on its surface when exposed to air. The affinity of this metal for oxygen is so great that strictly speaking it is not stable in air, but only remains unaffected because after the first thin film is produced oxygen no longer has access to it. In short-period exposure tests extending for 30 days Vernon (184) found that the increase in weight with time did not show a parabolic relationship. During the initial stages oxidation was more rapid than the parabolic law requires, and thereafter was much slower. The shape of the oxidation-time curves was therefore similar to those representing the attack of synthetic atmospheres on copper shown in Fig. 203.

There is no doubt that films are formed during the oxidation of aluminium, but the departure from the parabolic law shows that its progress is not controlled by diffusion through the film in the same way as in other metals. Vernon considers that it is not merely a coincidence that the oxidation-time curves of this metal are similar in form to those representing the velocity of adsorption of gases by such substances as charcoal, celluloid, glass, and alumina, and he suggests that it is adsorption rather than diffusion that controls the oxidation in this case. Whatever the explanation of the shape of the curve may be, the fact that it becomes substantially parallel to the time axis after about 10 days' exposure shows that an extremely impervious film is formed.

In experiments extending over longer periods it was found that the oxidation rate was not affected by seasonal changes in the atmosphere, but that there were periodic increases in the rate of attack due to spontaneous cracking of the film. This is illustrated in Fig. 206 which shows weight-increment time curves for an exposure of 90 days. After certain intervals during which the curve is virtually flat a sudden increase in oxidation takes place as a result of cracking, but in a comparatively short time the curve again becomes horizontal as a result of the 'healing' of the film. Despite these temporary increases in the rate of oxidation the total amount of oxide produced on aluminium is very small as is shown by the fact that the increase in weight after 90 days' exposure

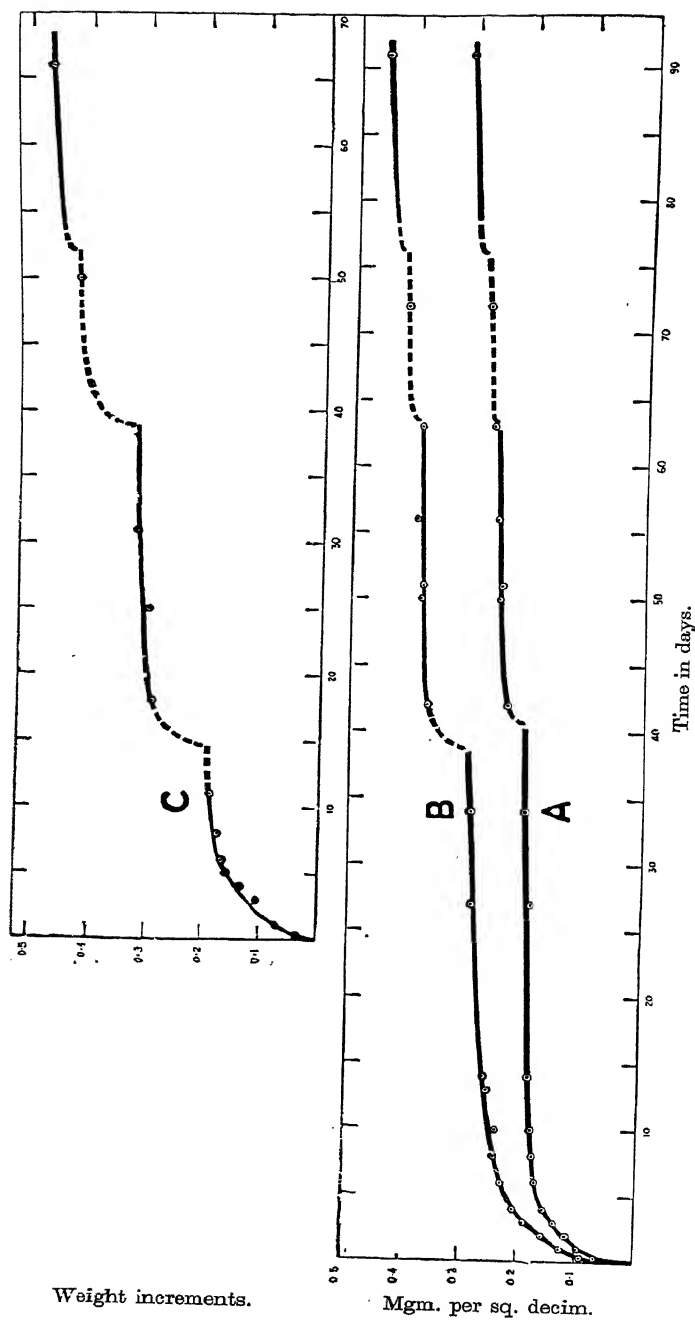


FIG. 206. Oxidation of aluminium at the ordinary temperature. Weight-increment curves ('Long Period'). Partly hypothetical. Curve *C* was started at a later date than *A* and *B* and is placed in the appropriate position.
(*Journal of the Faraday Society.*)

was 0.31 mg. per 100 sq. cm. compared with an increase of 2.0 mg. in the case of copper and 1.8 mg. in the case of zinc.

The oxidation-time curves of lead were found to be similar in shape to those of aluminium, and corresponding periodic increases in the rate of oxidation were observed. The time required after exposure for the curve to become parallel to the time axis was less in the case of lead than in that of aluminium, and furthermore, the increase in weight up to this time was also less, being 0.1–0.15 mg. per 100 sq. cm. for lead and 0.14–0.24 mg. per 100 sq. cm. for aluminium. Very rapid corrosion of freshly cleaned lead was observed when the atmosphere was contaminated with traces of the vapour of drying paint. None of the other metals exhibited this effect, neither did lead which had previously been exposed long enough to develop a protective film.

Iron.

In the basement where Vernon's experiments were carried out the mean relative humidity was 68 per cent. in the summer period and 43 per cent. in the winter period. The atmosphere was consequently always above the dew-point and no direct condensation of moisture occurred. In such an atmosphere iron should not rust, but in practice it does so, and the attack is due to deposition on the iron of hygroscopic solid particles carried by the atmosphere. The controlling influence of such particles is shown by some experiments carried out by Vernon. Two specimens of commercially pure iron were exposed simultaneously in the winter period. One was unprotected from the deposition of dust; the other was surrounded by a muslin screen. Rusting soon began at certain spots on the unprotected specimen and continued by an increase in the number of spots until they covered the whole surface with the exception of narrow bands of unaffected iron that separated the rust spots from each other. In 92 days the weight increased by 2.2 mg. per 100 sq. cm. The specimen protected by the muslin screen was quite unaffected by the same exposure, thus showing that deposition of solid particles was the cause of the rusting of the unscreened specimen.

The weight-increment curve for the unprotected specimen was approximately parabolic, indicating that the rate of rusting tended to decrease with time. In this case, however, there was no question of film formation and the decrease in rate was evidently due to a decrease in the area of unaltered metal on which further deposition of hygroscopic solid particles could occur. In the winter period therefore when the humidity was low the rate of attack on the iron was controlled by the rate of deposition of dust on the unattacked parts of the metal.

The atmosphere in the basement during the summer was more humid than during the winter but the temperature was always above the dew-point. Consequently, no direct condensation took place. When unprotected specimens were exposed in the summer, rusting proceeded slowly despite the greater humidity, for the rate of deposition of dust

was slower in the summer than in the winter. The conditions were quite different, however, when a specimen previously exposed in the winter passed into the summer period. During the winter period this specimen became covered with rust due to the deposition of hygroscopic dust, but the rate of rusting was comparatively slow because the critical humidity of the corrosion product was not reached. On passing into the sum-

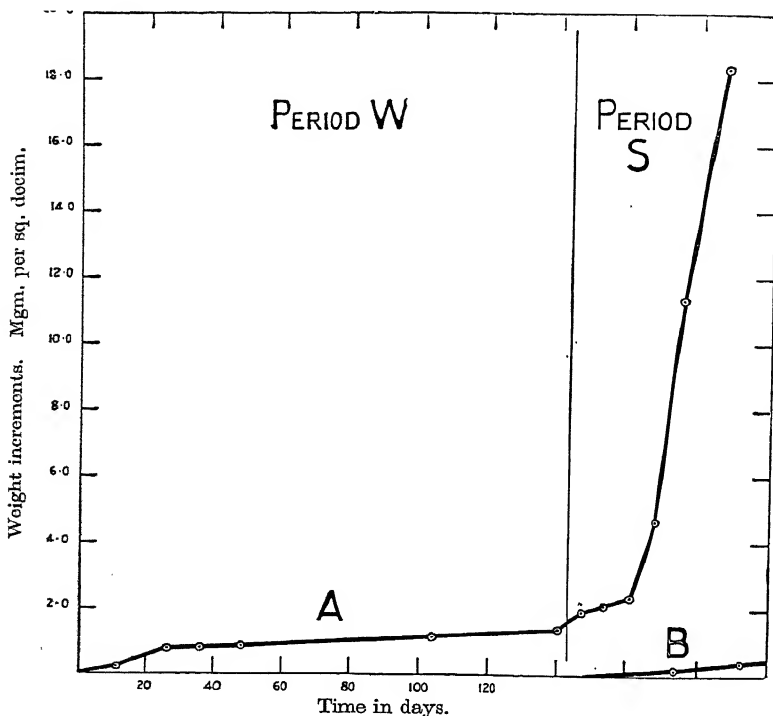


FIG. 207. *A*—Effect of increase in atmospheric humidity (Period S) upon iron which has already rusted in a relatively dry atmosphere (Period W).

B—Intrinsic effect of the more humid conditions upon freshly cleaned iron.

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mer, however, it was exceeded, moisture was readily taken up by the corrosion product, and the attack was greatly accelerated. This is shown by Fig. 207 in which curve *A* represents the weight increments of a specimen exposed for 140 days in the winter period before passing into the summer. Curve *B* is the weight-increment curve for a freshly cleaned specimen first exposed in summer.

The specimen exposed behind muslin during the winter period was quite unaffected by the change in atmospheric conditions in the summer. There was no visible rusting of the surface and the weight continued to increase at a negligible rate. After 159 days' exposure (96 in winter and 63 in summer) the weight increment was 0.2 mg. per 100 sq. cm. whereas

that for an unprotected specimen simultaneously exposed was 48.5 mg. per 100 sq. cm. The small increase in weight of the protected specimen was evidently due to the building up of a protective film, and when it was taken from the muslin screen after 314 days and exposed in the ordinary way it showed a much greater resistance to corrosion than did a freshly cleaned specimen simultaneously exposed. Rusting did eventually begin, but its subsequent course was quite different from that which obtained in other cases. Beginning at a few isolated spots, it continued by the intensification of the attack there rather than by the formation of new ones, and it appears that the points at which rusting began were cracks in the otherwise protective film. After 140 days' ordinary exposure this specimen had increased in weight by 0.39 mg. per 100 sq. cm. whereas the weight increase in the corresponding period of a specimen on which no protective film had developed was 1.42 mg. per 100 sq. cm.

These experiments on the effect of the atmosphere on commercially pure iron may be summed up as follows:

1. When protected from hygroscopic dust and exposed to an atmosphere that does not fall below the dew-point a fairly protective film is formed.
2. When protected from dust and exposed to dew-point conditions electrochemical corrosion takes place.
3. When exposed in the ordinary way to an atmosphere that does not fall below the dew-point rusting is controlled by the deposition of hygroscopic dust. In the early stages of exposure the humidity of the atmosphere has little effect on the rate of change, but once the surface has become virtually covered with rust the subsequent rate of corrosion is profoundly affected by the humidity. If the critical humidity of the corrosion product is not exceeded, rusting is comparatively slow; if it is, the change is very rapid.

In a further investigation Vernon (198) deals with the oxidation and rusting of iron in atmospheres of various degrees of humidity and contamination. He shows that the film formed on iron in purified air at temperatures below 200° C. is completely different from that formed at higher temperatures. Below 200° C. interference colours are not produced and film thicknesses which give colours above 200° C. may be greatly exceeded without appreciable change in the appearance of the metal. It appears that the film formed below 200° C. is granular (discontinuous), while that formed above 200° C. is continuous. In experiments at 25° C. abrupt changes in the rate of oxidation were observed after 15 days, and again after 35 days. The first change is believed to mark the stage at which the surface becomes completely covered with an oxide film; the second change occurs when the film becomes too thick to remain continuous and breaks down to a granular layer. This appears to be the usual sequence of events in the formation of granular films as explained at the beginning of this section, and the peculiarity of iron seems to

arise from the fact that the continuous film formed attains an appreciable thickness and a certain protective value before it breaks down under stress and becomes granular. Thus iron exposed to dry air and screened from hygroscopic dust develops a layer that exerts a certain amount of protection, but owing to the periodic disruption of this into a granular layer the protective value never becomes pronounced. At atmospheric temperature iron differs from copper in that oxidation does not lead to the progressive building up of a protective film, and it differs from zinc in that the continuous film formed before break-down into a granular layer occurs attains some protective value. Above 200°C . the oxidation of iron leads to the progressive formation of continuous films, and zinc also behaves in this way at temperatures near its melting-point. This change over from granular to protective films with rising temperature is evidently due to the increased plasticity of the oxide, and although the change has little practical value in so far as pure zinc is concerned it has an important effect on the oxidation of brass at elevated temperatures. As will be shown later, the rate of oxidation of brass at such temperatures decreases to a pronounced extent when the zinc content is high enough to lead to the formation of an oxide film consisting of zinc oxide only.

In the report just referred to Vernon also deals with the effect of humidity, sulphur dioxide, and carbon dioxide on the oxidation and rusting of iron. The presence of small amounts of sulphur dioxide was found to increase the rate of rusting, but carbon dioxide is definitely shown to retard it. This result is of exceptional importance because carbon dioxide has for long been regarded as an active stimulator of the rusting of iron. It is true that fairly high concentrations of carbon dioxide in water produce more rapid corrosion than distilled water, but in atmospheric corrosion concentrations of this gas equal to, and many times greater than, the normal atmospheric content, actually retard corrosion.

Oxidation at Elevated Temperatures.

The noble metals silver, gold, platinum, palladium, &c., which do not react with the atmosphere at ordinary temperature are not appreciably oxidized at elevated temperatures. This is due to the high dissociation pressure of their oxides. When metal, oxide, and oxygen are present, and the oxygen pressure is higher than the dissociation pressure of the oxide the oxide is stable and metal is oxidized. If, however, the oxygen pressure is lower than the dissociation pressure of the oxide, the metal is not oxidized and the oxide dissociates. Oxide dissociation pressures increase with temperature, but in the case of the common metals they are negligibly small compared with the oxygen pressure of the atmosphere and do not affect the oxidation of these metals when solid. The dissociation pressures of the oxides of the noble metals are much higher and approach or exceed the oxygen pressure of the atmosphere

at temperatures below the melting-points of the metals which are consequently not oxidized when heated. Another phenomenon that influences oxidation is the volatility of the oxide, and when the metal molybdenum is heated in a current of air the oxide vaporizes as it forms, and the surface of the metal remains bright while its cross-sectional area is progressively reduced.

In so far as the common metals are concerned dissociation pressures and volatility are not important, and oxidation at elevated temperatures proceeds in much the same way as at atmospheric temperature, i.e. it depends in the first place on whether a granular discontinuous layer or a compact film is formed, then on the rate of diffusion through continuous films and the cracking of these films, and finally on the sintering of either granular or moderately compact films. Sintering is usually brought about by heating above a certain critical temperature, but it may also be produced by prolonged heating at a lower temperature. Metals which form oxides that undergo such a change may be expected to exhibit an alteration in the rate of oxidation when heated above a certain temperature or for more than a certain time at a lower temperature. Thus some metals give linear oxidation-time curves at low temperatures and parabolic curves at higher temperatures, and in others, oxidation may take place according to the parabolic law in the early stages of exposure and become substantially slower later on. Sometimes, the presence of small quantities of impurities is instrumental in promoting sintering, e.g. the sintering of oxide films on chromium is promoted by the presence of small amounts of water vapour.

Rate of Oxidation and Temperature.

The rate of combination between metals and oxygen and the rate of diffusion through oxide films increase with rising temperature, and this effect is well illustrated by Fig. 208 which shows the oxidation-time curves of electrolytic iron at a series of temperatures as determined by Portevin, Prétet, and Jolivet (199). The effect of temperature is also illustrated by the following table which shows the change with temperature of the rate constant K as determined by Pilling and Bedworth (183).

TABLE 44

Effect of Temperature on the Rate Constant of Copper

<i>Temperature ° C.</i>	<i>Rate Constant K.</i>
400	0.000000164
500	0.000000193
600	0.00000113
700	0.00000586
800	0.0000314
900	0.000127
950	0.000268
1,000	0.000602

From the consideration of his own and other work Dunn (200) found that the variation of the rate of oxidation with temperature could be expressed as follows:

$$\text{oxidation rate} = A_e \frac{-Q}{RT}$$

where T = absolute temperature, and A , Q , and R are constants.

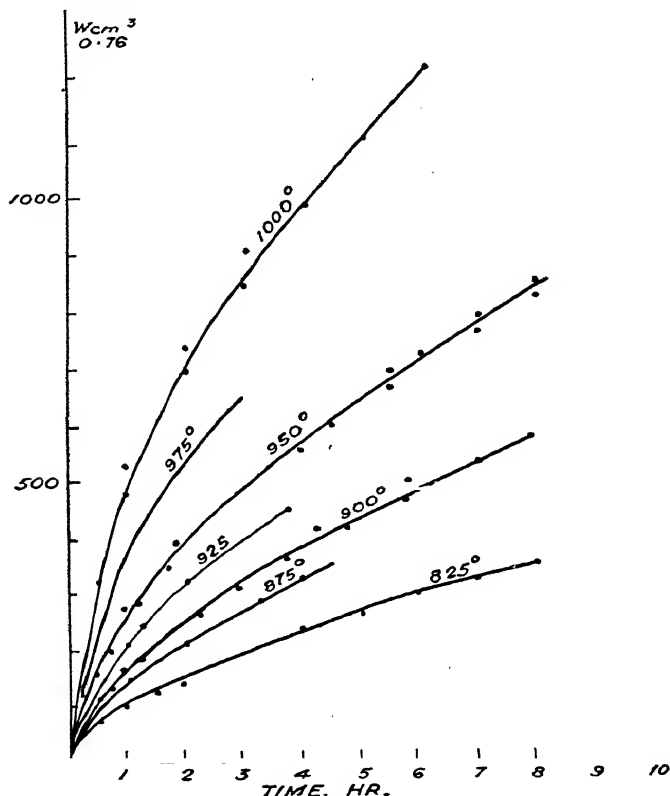


FIG. 208. Oxidation-time curves for electrolytic iron at different temperatures.

(*Journal of the Iron and Steel Institute.*)

Subsequent investigations have confirmed this relationship which therefore appears to be quite general and from which it follows that the log of the amount of oxygen absorbed gives a straight line when plotted against the reciprocal of the absolute temperature.

Rate of Oxidation, Oxygen Pressure, and Velocity of Flow.

The principal atmospheres to which metals are subjected during use at elevated temperatures are (1) air containing the usual impurities and at atmospheric pressure, (2) the products of combustion of different fuels also at or about atmospheric pressure, and (3) superheated steam

at high pressure. In the course of the fabricating operations which involve heating in furnaces and mechanical shaping in the air, hot metals are exposed to the action of air, the products of combustion of fuels, unburnt gas, and synthetic atmospheres of hydrogen, nitrogen, or hydrogen and nitrogen. The principal oxidizing constituents of these different atmospheres are oxygen, water vapour, and carbon dioxide, but sulphur dioxide which is present in furnace atmospheres is also important in this respect.

The partial pressure of one constituent of a gas mixture is proportional to its concentration, and as there are wide variations in the concentration of the oxidizing gases in the atmospheres to which metals are exposed, the effect of partial pressure is important. The basic atmosphere with which others should be compared is pure oxygen at atmospheric pressure. But owing to the fact that such an atmosphere is not realized in practice, much of the work on oxidation of metals has been done in air, in mixtures of air and the products of combustion, or in mixtures of the products of combustion and unburnt gas. Pilling and Bedworth, however, studied the effect of different oxygen pressures which were obtained by dilution with inert gases or by direct variations of pressure. When the former method was used it was found that very dilute mixtures had to be supplied at a higher rate of flow in order to prevent a falling-off in the rate of oxidation through deficiency of oxygen at the metal surface.

The partial pressure of oxygen in the atmosphere is 150 mm. When Pilling and Bedworth compared the effect of air with that of oxygen at atmospheric pressure on the oxidation of copper at 700°, 800°, 900°, and 1,000° C., they found that when the oxygen pressure was thus increased from 150 to 710 mm., it produced no change in the essential mechanism of oxidation, and the difference in the quantitative results was small in comparison with the change in oxygen pressure. Further experiments were then carried out in which the oxygen pressure was varied directly, and the rate of oxidation of copper at 800° C. under different pressures determined. It was found that decreasing the oxygen pressure from 710 mm. down to 0.3 mm. was accompanied by a slow change in the rate of oxidation such that the rate at 0.3 mm. was 60 per cent. of that at 710 mm. Below 0.3 mm., however, the rate of oxidation decreased with great rapidity approaching zero for zero pressure. As far as copper at 800° C. is concerned, an oxygen pressure of 0.3 mm. is a critical value. Increasing the pressure above this has only a slight effect, decreasing the pressure below it has a profound effect. Using another method Pilling and Bedworth determined the critical oxygen pressures for nickel and iron at 800° C., and found these to be 0.04 and 0.22 mm. respectively.

The existence of a critical oxygen pressure throws some light on the mechanism of oxidation. The parabolic relation between oxidation and time shows that the process is controlled by diffusion through a

film which exerts an effect in proportion to its thickness. Since metal is present in excess on the inner surface of the oxide, the oxygen pressure in contact with the metal must be kept near to a constant low value which is the dissociation pressure of the oxide. The rate of diffusion through a membrane depends on the specific resistance to diffusion of the substance and the difference in pressure or concentration between the two sides. As the concentration of oxygen on the inside of the film and the specific resistance of the film to diffusion may be assumed to be fairly constant, the rate of oxidation might be expected to increase with the external oxygen pressure. The fact that it does so up to a certain low pressure, i.e. the critical pressure, and is then substantially constant, shows that the external pressure does not have a direct influence on the process. It appears that the third factor in the process is the capacity of the outer layer of oxide to dissolve oxygen, and the rate of diffusion is therefore controlled by the difference in the concentration of dissolved oxygen in the outer and inner layers respectively. So long as the supply of oxygen is sufficient to maintain the surface layer of oxide in a saturated condition, variations in pressure have little effect, but whenever the supply becomes inadequate to maintain the saturated condition, the rate of diffusion, and therefore the rate of oxidation, fall off with the oxygen pressure. The properties of the oxide which determine the rate of diffusion of oxygen are therefore (a) its dissociation pressure, (b) its saturation concentration of oxygen in solution, and (c) its specific resistance to diffusion. It will be shown later that in the oxidation of iron and steel the inward diffusion of oxygen is accompanied by the outward diffusion of metal and this is probably the case for other metals also. This counter-current diffusion of metal must affect the final result, but it does not alter the general features of the phenomenon.

As the rate of oxidation depends to a certain extent on the outer layer of oxide being maintained in a saturated condition with respect to oxygen it follows that the rate of flow of the oxidizing gas must have an effect under certain conditions. Murphy, Wood, and Jominy (201) studied the effect on steel at $1,250^{\circ}\text{C}$. of air, steam, and carbon dioxide flowing over the metal at different rates. For all three gases they found that, beginning with a very small rate of flow, the speed of oxidation increased rapidly with the rate of flow up to a critical rate, beyond which further increase had no effect. In the case of air and carbon dioxide the critical rate was very sharply marked; above a flow of about 3 to 5 cubic feet per minute no further increase in rate of oxidation occurred although the rate was increased to 950 cubic feet per minute. With steam the rate of oxidation increased gradually as the rate was raised from zero to a flow of about 18 feet per minute. Further increase in the rate was not accompanied by any increase in the rate of oxidation.

OXIDATION OF NON-FERROUS METALS AND ALLOYS

It has already been shown that the oxidation of copper at atmospheric temperature conforms to the parabolic law, and with certain reservations this applies generally to all temperatures up to the melting-point as shown by the investigations of Pilling and Bedworth (183), Vernon (202), Hudson, Herbert, Ball, and Bucknall (203), and Wilkins (204).

Pilling and Bedworth studied the oxidation of copper at 400°, 500°, 600°, 700°, 800°, 900°, and 1,000° C. They found that at 800° and all higher temperatures the parabolic law was obeyed without reservation, but that at 700° C. and all lower temperatures abnormalities appeared in the curves. The continuous oxidation curve at 500° C. resembled, to some extent, that of the oxidation of aluminium at atmospheric temperature (Fig. 206). In the early stages it conformed to the parabola, but after 25 minutes it suddenly accelerated, then became slower, then accelerated again at 50 minutes, and again became slower, and so on. From this it was inferred that in the range between 400° and 700° C. periodic cracking of the oxide occurred, thus leading to temporary acceleration in the rate of oxidation and to a marked increase in the amount of oxide formed in a given time. The appearance of the oxide coatings confirmed this inference, for whereas the coatings formed at 800° C. and above were smooth, those formed at 700° C. and below were rough and irregular with many longitudinal seams. Pilling and Bedworth concluded from this that from 800° C. upwards, the oxide was sufficiently plastic to permit of the continuous formation without cracking of oxide occupying more space than the metal from which it was formed, whereas at lower temperatures the brittleness of the oxide resulted in periodic cracking. The absence of cracking at temperatures below 300° C. is of course due to the extreme thinness of the films, but as these become thicker with time a sufficiently long exposure at 300° C. might eventually result in cracking. Hudson, Herbert, Ball, and Bucknall studied the oxidation of copper up to 600° C. and found it to be parabolic and regular, i.e. they did not obtain the deviations due to cracking observed by Pilling and Bedworth.

The effect of temperature on the rate of oxidation of copper is represented with fair accuracy by the equation already mentioned, but when the results of the various experimenters are plotted in the form $\log K$ against $1/T$ it is found that they do not all lie on one straight line from 20° to 1,000° C. From 20° to 600° C. the plot gives a straight line, and from 600° to 1,000° C. another straight line is obtained, but the two lines are not continuous and intersect at 600° C. Values for the oxidation-rate constant K of copper collected by Dunn and Wilkins (205) are given in Table 45.

By comparing the effects of dry and saturated oxygen Pilling and Bedworth showed that the presence of water vapour is without influence on the rate of oxidation of copper at elevated temperatures, and

TABLE 45

Oxidation-Rate Constant K of Copper

$$K = \frac{W^2}{t} = \text{gm.}/\text{cm.}^2/\text{hr.}$$

<i>Temperature ° C.</i>	<i>In air</i>	<i>In oxygen</i>
50	..	2.5×10^{-15}
100	..	1.6×10^{-13}
200	..	4.1×10^{-11}
300	6.6×10^{-10}	..
400	1.64×10^{-8}	0.72×10^{-8}
500	1.93×10^{-7}	0.42×10^{-7}
600	1.13×10^{-6}	0.32×10^{-6}
700	5.86×10^{-6}	2.68×10^{-6}
800	3.14×10^{-5}	2.70×10^{-5}
900	1.27×10^{-4}	1.10×10^{-4}
1,000	6.02×10^{-4}	4.60×10^{-4}

other work has shown that this applies to all other gases except those containing sulphur and chlorine. Sulphur compounds exert a slight accelerating effect, while chlorine compounds exert a marked effect.

The oxidation of nickel has been studied by Pilling and Bedworth and Dunn (see (205)), and within the range of temperature investigated it has been shown to obey the parabolic and exponential law connecting oxidation with time and temperature respectively. Values for the oxidation-rate constant K are as follows: 800° C., 0.093×10^{-6} , 900° C., 0.76×10^{-6} , 1,000° C., 3.4×10^{-6} , 1,100° C., 13.3×10^{-6} , and from these it will be seen that the oxidation of nickel is much slower than that of copper. A feature of the oxidation of nickel is the preferential oxidation at grain boundaries resulting in the oxide being pegged firmly into the metal (Dunn and Wilkins). As a result, the scale is tightly adherent and cannot be flaked off. It is not certain, however, that this would occur with absolutely pure nickel. This metal is specially sensitive to the action of chlorine compounds in the neighbourhood of 800° C., the accelerating action falling off rapidly as the temperature is raised above this. At 800° C. the rate of oxidation with air containing 5 per cent. of hydrogen chloride is 27 times greater than with ordinary air. At 900° C. it is only twice as great and at 1,000° C. the hydrogen chloride has little effect. These observations are consistent with the hypothesis of the formation of a loose structured nickel oxide at 800° C. and the sintering of this to a more compact and impervious form at higher temperatures.

Of the other metals, zinc has been shown to conform to the parabolic law at 400° C., and lead behaves in much the same way at 300° C. although oxidation is rapid. Cobalt and tungsten also oxidize parabolically, and the effect of temperature between 700° and 1,000° C. is in accordance with the exponential law. Aluminium and cadmium do not conform to the parabolic law and after the initial stage of oxidation is

passed no further increase in the thickness of the films occurs. In the experiments of Pilling and Bedworth the oxidation of aluminium at 600°C . was found to proceed at a perceptible rate for about 70 hours. Thereafter no further oxidation occurred during a total exposure of 900 hours. At 300°C . cadmium behaved in much the same way. The results obtained on aluminium at 600°C . are similar to those obtained at atmospheric temperature except that no cracking of the film occurs. This is presumably due to the greater plasticity of the film. Pilling and Bedworth explained the behaviour of aluminium by assuming that the initial increase in weight was due to the gradual formation of a film which, when once it extended over the whole surface, was absolutely protective. Evans and Dunn, however, consider that the pronounced difference in behaviour during the initial and later stages respectively is due to a change in the nature of the oxide brought about by prolonged heating. Magnesium and calcium do not obey the parabolic law but in contrast to aluminium and cadmium they continue to oxidize at the same rate during the whole time of exposure.

The oxidation of alloys is sometimes considerably more complicated than that of pure metals, and Dunn (206) has classified the various conditions that may be realized. In the first place alloys that consist of one constituent must be distinguished from those that contain two or more. In the former case the metals composing the alloy form a solid solution, and attention may first of all be confined to this type. If each of the metals is without action on the oxide of the other the film initially formed should consist of a solid solution of oxides, in which the metals are present in the same proportions as in the alloy. If this solid solution is chemically and physically stable the parabolic law should be obeyed throughout the process of oxidation. If, however, the oxide sinters, or undergoes any other physical change, or if a separation of phases or combination between the oxides occurs, then departures from the parabolic law in one sense or another may be expected. Different conditions are realized if one of the metals *B* is capable of reducing the oxide of the other metal *A*. In this case, if *B* can diffuse to the surface quickly enough to combine with all the oxygen reaching it, a film composed entirely of its oxide will form, and the parabolic law will be obeyed. If, however, *B* is present in small proportions, or if *A* is the more rapidly oxidized of the two metals, the diffusion of *B* will be unable to keep pace with the supply of oxygen at the surface. An oxide film containing both oxides will then be formed and the changes mentioned in connexion with the first case are possible. The conditions are again different when the alloy contains two constituents. In the initial stages these will be oxidized separately, but later on reactions between the oxides may take place leading to changes in the nature of the oxide layer and in the rate of oxidation.

Dunn investigated the behaviour of copper-zinc alloys containing up to 40 per cent. of zinc in the range of temperature between 600° and

900° C. In this range alloys containing less than 36 per cent. of zinc consist of one constituent, whereas those containing more consist of two constituents. It was found that the alloys consisting of one constituent could be divided into three groups on the basis of their behaviour when heated in oxygen. Those containing less than 14 per cent. of zinc oxidized at about the same rate as copper, the parabolic law was obeyed, and the resulting oxide layer contained the two metals in about the same proportions as the alloy. Those containing more than 20 per cent. of zinc all oxidized at the same rate which was only about one-eighth of the rate of those containing less than 14 per cent. of zinc. The product consisted almost entirely of zinc oxide, and the parabolic law was only approximately obeyed. The intermediate alloys containing 14 to 20 per cent. of zinc behaved abnormally. The parabolic law was not even approximately obeyed, the oxide layer contained both zinc and copper oxide, but not in the same proportions as the metals were present in the alloys, and the rate of oxidation decreased with increase in zinc content.

It was concluded that the departure from the parabolic law in the case of the alloys containing more than 20 per cent. of zinc was due to sintering of the oxide leading to a decrease in its permeability. To test this, one specimen was heated in oxygen for 1 hour, then in nitrogen for 2 hours, and then in oxygen for a further 3 hours. The increase in weight due to this treatment was 9.8 mg. compared with an increase of 17.2 mg. for a specimen heated in oxygen for 4 hours without interruption. It is evident from this experiment that a change in the direction of decreased permeability took place in this oxide, but it is also clear that it was greatly facilitated by the presence of nitrogen or the absence of oxygen. As the oxidation of these alloys was not appreciably more rapid in oxygen than in air, it seems unlikely that the nitrogen was the controlling factor, and Dunn concluded that the presence of oxygen in solid solution was responsible for preventing the sintering of the oxide.

On the alloys containing more than 20 per cent. of zinc the oxide coating consisted entirely of zinc-oxide. In order that such a coating may be formed it is evident that the diffusion of zinc to the surface must keep pace with the oxygen supply. As the zinc content of the alloy becomes smaller, the amount of this metal capable of reaching the surface by diffusion naturally becomes less, and when less than 20 per cent. is present it can no longer reach the surface sufficiently quickly to reduce all the copper oxide. In these circumstances a film rich in copper oxide is formed, and as this permits more rapid transmission of oxygen than a zinc-oxide film, the disparity between the supply of zinc and oxygen is further increased. Thus in the range of composition between 20 and 14 per cent. of zinc the rate of oxidation increases rapidly as the zinc content decreases, until with less than 14 per cent. of zinc a film that consists virtually of copper oxide is formed, and thereafter the rate of oxidation does not change with the composition.

The relations between the rate of oxidation and the composition can be explained by taking account of the diffusion of zinc, the reduction of copper oxide by zinc, and the greater permeability of copper oxide compared with zinc oxide. The relative proportions of zinc and copper in the oxide coatings may also be explained on this basis. But some other factor is required to explain the departure from the parabolic law in the case of the alloys containing between 14 and 20 per cent. of zinc. It appears that any zinc oxide on the alloys containing less than 14 per cent. of zinc is present in solid solution in the predominant copper oxide, and any copper oxide in the alloys containing more than 20 per cent. of zinc is in solid solution in the predominant zinc oxide. Between these limits both oxides are present as separate phases. In the early stages of oxidation this two-phase oxide layer is fairly pervious, but later, as a result of some reaction between them it becomes impervious and a pronounced departure from the parabolic law is the result.

Dunn also investigated the effects of atmospheric impurities and the addition of certain elements to the metal. Water vapour, carbon dioxide, and dry sulphur dioxide were found to have no accelerating effect on the rate of oxidation. Wet sulphur dioxide caused a considerable increase in oxidation, but the most active impurity proved to be hydrogen chloride, which is now known to accelerate the oxidation of most metals. Below a concentration of about 5 volumes in 10,000 hydrogen chloride proved to have no appreciable effect on an alloy containing 40 per cent. zinc at 725° C. Above this, however, the rate of oxidation increased, and 7.5 volumes in 10,000 caused a fivefold increase in the rate of oxidation. The effect of the hydrogen chloride appears to be catalytic, and similar effects are obtained with a number of metals when exposed to atmospheres containing chlorine or compounds of chlorine. The increased rate of oxidation is due to the formation of an oxide of loose structure which is abnormally permeable to oxygen. In the case of nickel, if the temperature is maintained high enough the loose structured oxide sinters almost immediately to a compact form and the catalytic effect of chlorine compounds is almost entirely eliminated.

Among the common additions to brass are nickel and aluminium, whilst arsenic is frequently present as an impurity. The oxides of these three metals are typical of different classes. Arsenic oxide is volatile at high temperatures, nickel oxides are not volatile but are easily reduced, while aluminium oxide is non-volatile, impervious, and exceedingly difficult to reduce. Arsenic up to 0.2 per cent. and nickel up to 1 per cent. were found to be without influence on the rate of oxidation, but the addition of small quantities of aluminium was found to modify profoundly both the form of the oxidation curve and the actual rate of oxidation. The effect of aluminium on the amount of oxide produced in a given time is shown in Fig. 209. The addition of 1.9 per cent. reduces the oxidation rate to about one-fortieth of its original value, and after heating in oxygen for 18.5 hours at 775° C.

a specimen of this composition appeared unchanged except for a very slight loss of lustre and a faint temper colour. These results are in accordance with expectations. Any arsenic oxide formed would volatilize, nickel oxide would be reduced by zinc, but aluminium oxide would neither volatilize nor be reduced, it would tend rather to reduce

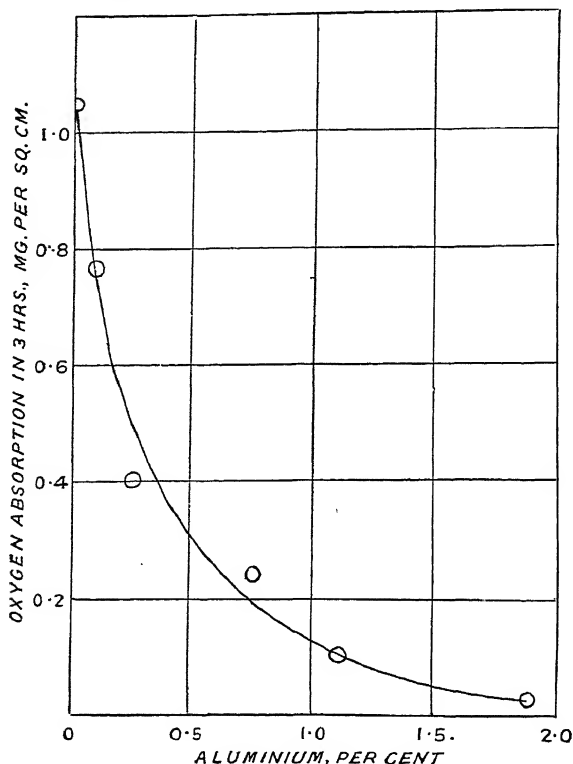


FIG. 209. Effect of aluminium on oxidation of brass.
(*Journal of the Institute of Metals.*)

the zinc oxide, thus giving rise to a film becoming progressively richer in alumina with increase in the aluminium content of the alloy.

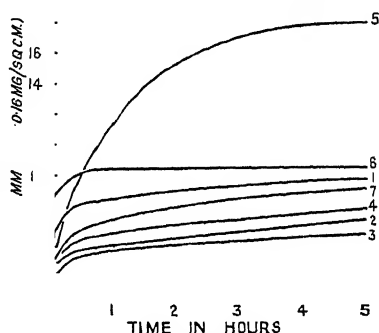
Pilling and Bedworth studied the oxidation of copper-nickel alloys and found that the copper rich alloys oxidized at rates similar to copper, while nickel rich alloys oxidized at rates similar to nickel. The alloys at each end of the system oxidized parabolically but those with 40, 50, and 60 per cent. of nickel were found to be abnormal and to have abnormal temperature coefficients. They oxidized similarly to nickel at lower temperatures and similarly to copper at higher temperatures. Dunn and Wilkins (205) describe some experiments on the copper-nickel alloy 'Corronil' (70 per cent. Ni, 30 per cent. Cu). At and below 850° C. this alloy obeyed the parabolic law for the duration of the test (4 hours), but at 900° C. and above, after a short period of normal parabolic

oxidation the resistance of the oxide film decreased considerably and the rate of oxidation increased. This increased rate soon diminished and oxidation appeared to follow another parabolic curve with a considerably higher value of K . The composition of the scale differed considerably from that of the metal. Experiments on copper-silicon alloys are also described by these authors. At 725° C. one containing 0.9 per cent. silicon oxidized parabolically and slightly less rapidly than copper, while alloys containing 3.25 and 4.58 per cent. oxidized irregularly (giving parabolic curves with breaks) and much more slowly than copper. At 827° C. these two alloys of high silicon content began to oxidize slowly, but later there was a sudden increase in the oxidation rate which then became similar to that of copper. No silicon was found in the scale.

Nickel-chromium alloys containing more than 15 per cent. of chromium are highly resistant to oxidation at elevated temperatures and are used extensively where this property is required. The following figures given by Dunn and Wilkins for oxygen uptake (in mg. per sq. cm.) during the first two hours exposure at 1,000° C. indicate the effect of composition.

Composition % . 100 Ni, 5 Cr, 10 Cr, 15 Cr, 20 Cr, 30 Cr, 40 Cr, 100 Cr.
O₂ uptake . . 2.34, 3.12, 4.04, 0.84, 0.21, 0.18, 0.11, 1.6.

In the case of the highly resistant alloys the oxidation rate subsequent to the first two hours was much smaller. The fact that some of the alloys oxidize less rapidly than chromium suggests that the nickel promotes the sintering of the film of chromium oxide. In order to decrease the cost of the alloys iron is frequently added, and it tends to diminish the resistance to oxidation. Aluminium, on the other hand, tends to increase it. Utida and Saito (207) determined the oxidation-time curves for a series of these alloys. Their curves are reproduced in Fig. 210 and the analyses of the alloys are given in Table 46.



210. Oxidation-time curves of nickel-chromium alloys.

TABLE 46

No.	Trade name	Nickel	Chromium	Iron	Aluminium
		%	%	%	%
1	Nichrome	59.8	15.6	23.2	1.7
2	Nichrome 2	67.7	20.9	8.9	1.4
3	Kromore	80.2	17.8	1.1	3.1
4	Chromel A	75.5	18.5	4.0	1.0
5	Chromel C	62.0	10.4	25.6	1.2
6	Calido	62.7	11.8	23.0	1.6
7	Rayo	83.1	13.2	3.0	1.3

THE OXIDATION OF IRON AND STEEL

Iron, and ordinary varieties of steel and cast iron, oxidize rapidly at elevated temperatures. Because of this, substantial amounts of metal are lost during heating and hot-working operations, and when service temperatures over about 500° C. have to be withstood special heat-resisting alloys must be used. The rapid oxidation of ordinary ferrous metals is due to the ready solubility of both oxygen and iron in iron-oxide and the comparative rapidity of diffusion of these elements through the oxide layer. Four aspects of the oxidation of iron and steel may be distinguished and dealt with separately (1) the mechanism of oxidation, (2) the rate of oxidation, (3) the effect of the composition of the atmosphere, and (4) the effect of the composition of the metal. Other and more practical aspects such as control of the atmospheres in which steels are heated, and alloys used for high-temperature service, are considered in Chapters X and XIII respectively.

The mechanism of oxidation has been studied by Pfeil (208) and the following account is based on his work, the general features of which have been confirmed by subsequent investigators. As soon as the scale becomes sufficiently thick for microscopic examination to be practicable (about 0.004 inch) three layers of oxide can be distinguished on iron or steel heated at temperatures above 600° C. When it attains a thickness of 0.05 inch, the innermost layer can be separated from the other two and the metal, but the two outer layers cannot be separated from each other until a thickness of 0.147 inch is reached. This requires heating in air at 1,000° C. for about 46 hours. With sufficient care, uncontaminated samples of each layer can be obtained for analysis, and the results show that the iron content increases while that of the oxygen decreases as the surface of the metal is approached. The composition of the various layers is independent of the time of exposure and of the temperature, so long as it is above 600° C. All the layers consist of ferrous oxide (FeO) and ferric oxide (Fe_2O_3). In the outer layer these are present in the (approximate) proportions of 21 per cent. of FeO to 79 per cent. of Fe_2O_3 , in the middle layer the proportions are 71 to 29 per cent., and in the innermost layer they are about 82 to 18 per cent. About 10 per cent. of the total thickness of the scale consists of the outer layer, about 50 per cent. of the middle layer, and 40 per cent. of the innermost layer.

The scale does not invariably consist of three layers and three layers only. Where disturbing influences, such as blistering of the scale and serious temperature fluctuations, have been at work the number of layers may be more or less than three. In general, however, three layers are formed, the outer and middle layers being dense, and breaking with a conchoidal to crystalline fracture, whereas the innermost layer is weak and porous and may be powdered between the fingers. All the details of the surface of the original specimen, such as identification

numbers, sawmarks, &c., are shown perfectly in reverse on the inner surface of the middle layer. This indicates that this is the thin film formed when the metal is first exposed.

The mechanism of the growth of scale on iron and steel is clearly indicated by the following experiment carried out by Pfeil. A thick-walled iron tube of 0.5 inch, external diameter and 0.19 inch bore, was heated in air at 900° C. for 6 days. By this time the bore was completely filled with scale while a thick deposit on the outside of the tube increased its external diameter to 0.6 inch. The scale on the outside of the tube consisted of the three layers just described, whereas that in the inside consisted of a solid rod of the same diameter as the original bore of the tube, and a loose deposit of crystals filling the annular space between the rod of scale and the inner surface of the corroded tube. When the tube was first exposed, a thin layer of oxide would form both on the inner and outer surface, and if the subsequent thickening of the scale depended entirely on the inward diffusion of oxygen, the original film on the outside would require to be expanded to a diameter of 0.6 inch, while that on the inside would have to be compressed to form the centre of the solid rod. At temperatures in the neighbourhood of 1,000° C. scale is not plastic enough to undergo this amount of deformation, and in any case the porous loose-textured scale adjacent to the metal could not exert sufficient pressure to deform the dense scale of the outer layers. Furthermore, the inner surface of the middle layer of the scale on the outside of the tube conforms to the original external diameter and bears the impression of any markings on the original surface, while the outer surface of the solid rod of scale conforms to the original internal diameter and retains the impression of any markings on the original inner surface. Therefore, it must be concluded that the inner surface of the middle layer of scale on the outside of the tube, and the outer surface of the solid rod of scale in the inside of the tube, are the first oxide layers that were formed, and that subsequent thickening takes place in both directions from the original film.

The growth of scale on iron and steel at temperatures above 600° C. may therefore be described in the following way. When the metal is first exposed a thin layer of oxide is formed on the surface. This is capable of dissolving both iron and oxygen. On the outer surface in contact with air oxygen is dissolved. This diffuses through the scale and combines with iron on the inner surface. The mechanism is thus the same as that already described in connexion with the oxidation of copper. At the same time, however, iron dissolves at the inner surface of the scale and diffuses outwards to the surface where it is converted to iron oxide. Thus thickening of the scale takes place in both directions from the original film. Pfeil's experiments have shown that this is the mechanism of growth of thick scales on iron and steel. A similar process almost certainly occurs during the formation of thinner scales at lower temperatures on iron and other metals.

It is evident that the building up of a dense layer of scale without cracking would involve a very nice adjustment between the amount of iron diffusing outwards and that of oxygen diffusing inwards. Under the requisite conditions this result might be attained, but in general there is more outward than inward diffusion, and consequently dense scale is formed outside the original film, while porous scale is formed inside it. The presence of certain elements in the metal or on its surface leads to a modification of the process. Pfeil found that when specimens were coated with a wash of litharge and water and heated at $1,000^{\circ}\text{C}$. for 96 hours the outer layers of oxide were cracked and swollen instead of being dense and smooth. This was evidently due to the fact that the lead in the first scale layer had delayed the outward diffusion of iron and not the inward diffusion of oxygen. Thus the space occupied by the oxide formed under the original layer was greater than that left by the iron diffusing outwards, with the result that periodic cracking of the outer scale occurred. In other experiments under less definite conditions the balance of diffusion rates was displaced in the other direction, outward diffusion being accelerated relative to inward diffusion. As a result, certain specimens after three days' exposure revealed a hollow space between the metal and the scale. Other evidence suggested that this condition was not maintained throughout the whole time of exposure, and that the hollow space was at other periods occupied by loose textured oxide.

The rate of oxidation of iron and steel and the effect thereon of temperature and atmosphere has been studied by a number of investigators and a considerable amount of the existing information is reviewed by Hudson and Rooney (209). For the purpose of their review these authors found it possible to neglect the effect of variations in composition such as occur in ordinary carbon steels or when small amounts of alloying elements are added for reasons other than the prevention of oxidation and corrosion. They were thus able to generalize on the basis of work done on alloys of varying composition. Their survey shows that the oxidation-time curves for iron and steel in air and oxygen may, for practical purposes, be regarded as parabolic, and that deviations from this may be attributed to cracking and to the complex composition of the scale. Portevin, Prétet, and Jolivet (199) reached the same conclusion from carefully conducted experiments on electrolytic iron (Fig. 208) and attributed certain irregularities observed during the initial stages of oxidation to the original surface condition of the specimens. Hudson and Rooney concluded from their survey that the effect of temperature on the oxidation of iron and steel is in accordance with the exponential law, and this again is confirmed by Portevin, Prétet, and Jolivet.

In order to give a quantitative idea of the amount of metal oxidized during a constant time of heating at different temperatures, Hudson and Rooney reduced the results of a number of investigators to a

common basis, viz. the thickness of metal oxidized during the first hour of exposure. After tabulating the figures they arrived at a mean value for each temperature, and these values are given in Table 47.

TABLE 47

Rate of Oxidation of Iron and Steel at Various Temperatures

(Thousandths of an inch of metal per hour.)

Temperature ° C.	Mean rate	
	<i>In air</i>	<i>In oxygen</i>
550	0.07	..
600	0.08	..
650	0.14	..
700	0.34	0.64
750	0.65	0.85
800	0.99	1.34
850	1.47	2.09
900	2.27	3.20
950	3.62	4.83
1,000	5.28	7.14
1,050	6.07	(8.60)
1,100	7.01	(9.46)
1,150	7.38	(12.10)
1,200	9.12	(15.00)
1,250	9.30	..
1,300	(10.00)	..

The figures in brackets are not mean values but are the single results available for these temperatures. The mean values shown may be used with a reasonable degree of confidence to compute the probable extent of oxidation of iron and mild steel in a stream of air or oxygen, the thickness of metal oxidized in a given period being obtained by multiplying the figures shown by the square root of the time in hours.

In practice, steel is not exposed to the action of pure oxygen. During hot-working operations it is exposed to air, but as the scale formed is continuously removed the conditions are different from those realized in laboratory experiments. The practical implications of the work done on oxidation are mainly related to heating operations in which the steel is exposed to air in electric furnaces (when no other atmosphere is provided) and to the products of combustion in fuel-fired furnaces. The temperatures reached in the heating operations to which steel is subjected are approximately as follows:

Heating for rolling or forging	1,250°–1,320° C.
Heating for quenching, normalizing or full annealing	760°–980° C.
Heating for low temperature annealing	680°–800° C.

and the gases to which it is exposed are various mixtures of nitrogen and oxygen in the air, hydrogen, carbon monoxide, and hydrocarbons in the fuel, and carbon dioxide, water vapour, and sulphur dioxide in the products of combustion. Of these gases oxygen, carbon dioxide,

water vapour, and sulphur dioxide are oxidizing, and when atmospheric control is resorted to in order to reduce oxidation the main object is to decrease the proportion of these gases in the furnace atmosphere. This may be accomplished in the first instance by decreasing the air supply so as to reduce the amount of free oxygen and the amount of carbon dioxide and water vapour formed. This of course reduces the thermal efficiency of the furnace, and there is a limit to the extent to which oxidation can be prevented by this method. Further restriction of oxidation involves providing an atmosphere that is independent of the source of heat. This and other methods of restricting or preventing oxidation will be discussed in Chapter X, meanwhile, attention may be confined to the general effects of different atmospheres.

As at least six gases have to be considered, and as the possible mixtures of these may vary widely, and have access to the steel at a variety of temperatures, a systematic account of the problem of atmosphere could not be undertaken here even if the necessary data were available. Furthermore, the prevention of oxidation is closely connected with decarburization which further complicates the subject. It will therefore be sufficient at present to give a general idea of the oxidizing effect of different individual gases and the part played by each in mixtures. It should be stated in the first place that at the high temperatures to which steel may be heated, carbon dioxide, water vapour, and sulphur dioxide are active oxidizing agents. Upthegrove (210) studied the effect of oxygen, air, carbon dioxide, steam, and various combustion atmospheres at temperatures ranging from 540° to $1,260^{\circ}$ C. Adopting a standard time of exposure of two hours and the oxidation of 0.0001 inch of metal as indicating appreciable oxidation he observed that this began at 700° C. in oxygen, at 670° C. in air, and at 600° C. in carbon dioxide and steam. The rate of oxidation increased with temperature, but the rate of this increase was slower in the case of carbon dioxide than in that of the other gases. Thus 0.001 in. of metal was oxidized in 2 hours at 790° C. in steam, at 850° C. in air and oxygen, and at $1,010^{\circ}$ C. in carbon dioxide. At $1,093^{\circ}$ C. (the highest temperature at which all gases were studied) the amounts of metal oxidized in 2 hours were, in order of increasing oxidation, carbon dioxide, 0.0049 inch, dry air 0.0052 inch, oxygen 0.0132 inch, and steam 0.0145 inch. Thus at this temperature steam is the most effective of the four. The effect of time was studied at certain temperatures by continuing the exposure up to 5 or 8 hours. It was then found that while the oxidation-time curves for air and oxygen were of the parabolic type those for carbon dioxide and steam were of the straight-line type. In a series of experiments in which the gases were diluted with nitrogen it was found that in the case of air and oxygen this had little effect until the oxygen concentration was reduced below 20 per cent., in the case of steam the effect of dilution was rapid when the steam concentration fell below 80 per cent., and in the case of carbon dioxide dilution slowly decreased the

rate of oxidation until 80 per cent. of nitrogen was present; further additions of nitrogen had a more pronounced effect. In experiments in combustion atmospheres it was found that altering the gas-air ratio so as to vary the combustion atmosphere from one containing 1 per cent. of carbon monoxide to one containing 1 per cent. of oxygen was accompanied by a great increase in the rate of oxidation. In some cases it had the effect of doubling or tripling the metal loss. The introduction of 0.1 to 0.2 per cent. of sulphur dioxide caused an appreciable increase in the rate of oxidation.

Similar experiments to those described above have been carried out by Murphy and Jominy (211). They also found that 0.1 to 0.2 per cent. of sulphur dioxide increased the rate of scaling and gave rise to the formation of oxysulphide inclusions in the outer layers of the metal. The deleterious effect of this gas increased with temperature and time but it was less marked in reducing than in oxidizing atmospheres. The experiments of these workers were extended to higher temperatures than those of Upthegrove, and they observed that above $1,260^{\circ}\text{C}$. in oxygen and $1,316^{\circ}\text{C}$. in air, the heat of oxidation was capable of raising the temperature of the steel considerably above that of the furnace. In this temperature range (about $1,300^{\circ}\text{C}$.) very similar oxidation-time curves were obtained for air, oxygen, steam, and carbon dioxide. Schroeder's experiments (212) confirmed Upthegrove's observations on the pronounced increase in the rate of oxidation resulting from altering the composition of the combustion atmosphere from a slight excess of carbon monoxide to a slight excess of free oxygen. He also found that while the scale formed in an atmosphere containing excess oxygen was easily removed that formed in one containing a deficiency could only be removed with difficulty. Pickling was necessary to remove the last traces and the surface of the metal was roughened.

In collaboration with Marson, Angus, and Blackburn, Cobb has published two papers (213, 214) dealing with the influence of atmosphere on the scaling of mild steel. In experiments involving 3 hours' heating at $1,000^{\circ}\text{C}$. it was found that at least 58 per cent. of carbon monoxide was required in a mixture of this gas with carbon dioxide in order to prevent oxidation, while to secure the same result in hydrogen-steam mixtures 50 per cent. of the former was required. The rate of oxidation proved to be eight times greater in steam than in carbon dioxide. Consequently, the first effect of progressive additions of hydrogen to a carbon dioxide atmosphere was to increase the rate of oxidation due to the formation of steam. A maximum was observed at 26 per cent. of hydrogen when the loss by oxidation was three and a half times that in an atmosphere of carbon dioxide only. Further additions of hydrogen decreased the oxidation and it was reduced to zero when 57 per cent. was present. In the case of carbon monoxide-steam mixtures 80 per cent. of the former was required to prevent oxidation. Starting with two combustion atmospheres, one containing 10 per cent. of carbon

dioxide, 10 per cent. of steam, and 80 per cent. of nitrogen, and the other containing 18 per cent. of carbon dioxide, 2 per cent. of steam and 80 per cent. of nitrogen, Blackburn and Cobb studied the effect of adding reducing gases. When specimens were heated in the above atmospheres for 3 hours at $1,000^{\circ}\text{C}$. without the addition of reducing gases the amounts of metal oxidized were 0.0020 inch in the first atmosphere, and 0.0011 inch in the second, thus indicating the greater effect of steam as compared with carbon dioxide. When reducing gases were added it was found that 29.7 volumes of hydrogen or 95 volumes of carbon monoxide had to be added to 100 volumes of the first atmosphere to prevent oxidation while the same result could be obtained in the case of the second atmosphere by the addition of 24.8 and 65.6 volumes respectively. Blackburn and Cobb concluded that the amount of reducing agent necessary to prevent oxidation or even to decrease it by half is much larger than could be used in ordinary practice when the heating value of the fuel has to be utilized. In a further series of experiments in which small amounts of oxygen were added to the combustion atmospheres it was found that, while oxygen additions of 1 per cent. or more caused a marked increase in oxidation, the addition of about 0.5 per cent. had no such effect. Experiments were also carried out on the effect of the addition of sulphur dioxide to the above combustion atmospheres, and some of the results were privately communicated to Hudson and Rooney. It was found that small amounts of this gas (up to 0.01 per cent.) had a very pronounced effect in increasing the rate of oxidation, but with larger additions the rate did not increase so rapidly with the sulphur-dioxide concentration.

The Effect of Alloying Additions.

Pfeil (208) investigated the oxidation of a number of alloy steels as follows: (1) 2.75 per cent. nickel, (2) 36 per cent. nickel, (3) 12.23 per cent. chromium, (4) 3.18 per cent. nickel, 0.85 per cent. chromium, (5) 5.5 per cent. tungsten, (6) 0.27 per cent. vanadium, (7) 3.07 per cent. manganese, and (8) 2.02 per cent. silicon. Specimens of these were heated at $1,000^{\circ}\text{C}$. in air until heavy scales were formed. In general, the time required to produce a given thickness of scale was greater than for carbon steels. In almost every case the scale consisted of three separable layers and examination showed that the inner surface of the middle layer corresponded to the first oxide film formed. Except in the case of manganese steels the two outer scale layers contained very small amounts of the alloying elements as compared either with the original steel or the innermost layer. On the other hand, this layer contained a greater proportion of alloying elements than the metal itself. There was no silicon either in the outer- or middle-scale layers on silicon steel, whereas in the innermost layer the ratio of silicon to iron was three times that in the metal. On the nickel steel there was no nickel in the outer layer, only a trace in the middle layer, while in the

innermost layer the ratio of nickel to iron was three and a half times as great as in the metal. The distribution of chromium in the scale formed on the chromium steel was similar to that of nickel in the nickel steel scale. On the tungsten and vanadium steels there were small amounts of the special element in the outer layers, considerable amounts in the middle layers, and in the innermost layers there was twice as much relative to the iron as in the metal. In the outer layer of the scale formed on the manganese steel the manganese to iron ratio was about two-thirds of that in the steel, while in the middle and innermost layers the ratio was a little higher than in the original metal. The nickel in the innermost layer of the scale formed on the nickel and the nickel-chromium steels was present as metallic nickel. All the other alloying elements were present as oxides.

The distribution of the alloying elements in the scale is easily accounted for in accordance with the mechanism of scale formation already described. The innermost scale layer consists of oxide formed *in situ* below the original film. The middle and outer layers consist of oxide formed outside the original film by the outward diffusion of metal. When the alloying element is incapable of dissolving in or diffusing through the oxide none of it appears in the outer or middle layers. As some iron is diffusing outwards while the remainder of the iron and all of the alloying element is being oxidized *in situ* to form the innermost layer, the relative proportion of alloying element in this layer is therefore increased. This is exactly what happens in the case of silicon which is completely insoluble in the oxide, and it is substantially what happens with nickel and chromium which are practically insoluble in the oxide. Tungsten and vanadium being soluble to some extent in the scale, and therefore capable of diffusing through it, are found in both the middle and outer layers, but as they diffuse less rapidly than iron their relative concentration in the innermost layer is greater than in the metal. Manganese is very soluble in the oxide and is therefore found in considerable quantities in all three layers.

The oxidation of the nickel steel differed in two respects from that of any of the other alloy steels and also from that of iron or plain carbon-steels. The nickel occurred in the metallic state in the scale, and there was marked penetration of oxide along the crystal boundaries below the scale layer proper. Both of these features are due to the fact that nickel has a lower oxygen affinity than iron. Owing to its readier reactivity with oxygen, and its greater solubility in the oxide layer, iron will tend to be more rapidly oxidized than nickel. As a result of this, the nickel will tend to accumulate in the metal in immediate contact with the oxide, and consequently further oxidation will be retarded. This concentration of nickel in the metal in contact with oxide will produce a concentration gradient therein with respect to nickel, and this element will therefore diffuse through the metal in order to produce uniformity of distribution. Soon after oxidation starts the concentration

of nickel in the metal in contact with oxide will become sufficiently great to prevent further oxidation at an appreciable rate. Thereafter oxidation can only proceed as nickel diffuses away from the oxide-metal interface. If there was no preferential oxidation along the crystal boundaries the oxide-metal interface would advance slowly as nickel diffused away until the concentration of nickel in the remaining metal became sufficient to prevent further oxidation. As a general rule, however, the boundaries of crystals are more susceptible to chemical action than the interiors. Consequently, when the regular advance of the oxide is delayed by the accumulation of nickel, oxygen penetrates along the crystal boundaries and iron oxide is formed. As a result, nickel accumulates in contact with the oxide at the crystal boundaries, and further oxidation only takes place as this diffuses towards the interior of the crystals. Thus the individual crystals are oxidized from all sides and the metallic particles in the inner-scale layer are the centres of the original crystals in which nickel has been concentrated to such an extent that no further oxidation can occur.

The scale formed on steel containing copper has been studied by Rådeker (215). Three scale layers were found as in the case of the alloys studied by Pfeil. Copper was present in the outer layers but in smaller concentrations than in the innermost layer. When the copper content of the steel exceeded 0.5 per cent., metallic copper was present in the innermost scale layer, but the ratio of copper to iron in the scale was less than in the metal, thus indicating that the metal was enriched in copper. Portevin, Prétet, and Jolivet studied the scales formed on alloys of iron with aluminium, chromium, and silicon which are the elements added to secure resistance to oxidation. Their general conclusions were similar to those reached by Pfeil, and they found that as the content of alloying element was increased the scales at first retained the characteristics of iron scales, then changed gradually to duplex mixed systems of oxides, and finally consisted mainly of oxides of the alloying elements. The amount of alloying element required to produce a scale rich in its oxide was found to increase with the temperature of heating and to vary with the atmosphere.

From the above experimental results it may be concluded that the distribution of an alloying element in the scale is not a function of its affinity for oxygen, and it seems most probable that the distribution is due to the relative rates of diffusion of iron and the alloying element in the scale. Iron-oxide scales permit easy diffusion of iron and oxygen, but the diffusion of alloying elements in such scales varies considerably. Thus, nickel and silicon have a negligible capacity for diffusion, while chromium, tungsten, vanadium, copper, and manganese are able to diffuse to some extent but not so rapidly as iron. As the amount of alloying element increases, the constitution of the scale alters, and it becomes more resistant to the diffusion of iron and oxygen. The rate of oxidation therefore decreases, and when the conditions are such that

scales consisting mainly of oxides of chromium, silicon, or aluminium are formed, it is reduced to a low value.

Portevin, Prétet, and Jolivet determined oxidation-time curves for various series of alloys of iron with aluminium, chromium, and silicon respectively at 900° and 1,000° C. Their curves for electrolytic iron and a series of alloys containing 2.5 to 8.5 per cent of aluminium at 900° C. are shown in Fig. 211 from which the effect of aluminium in decreasing the rate of oxidation will be seen. Up to 5 per cent. of aluminium the curves have a similar parabolic form to those of pure iron. Above this

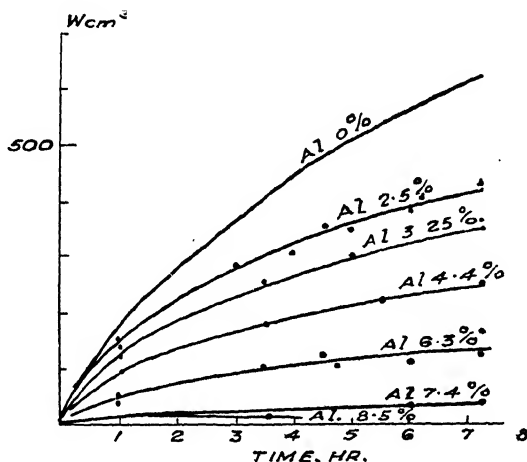


Fig. 211. Oxidation-time curves of iron-aluminium alloys at 900° C.

(*Journal of the Iron and Steel Institute.*)

amount a definite departure from the parabolic form is observed. Similar sets of curves were determined for aluminium alloys at 1,000° C. and for chromium and silicon alloys at 900° and 1,000° C. The curves for alloys of low chromium content were parabolic, but above 6 per cent. this form of curve was not maintained. With chromium contents between 15 and 30 per cent., after a short initial period when the oxidation was measurable, it became very slow. The curves for the iron-silicon alloys retained the parabolic form up to about 5 per cent. Comparing the effect of aluminium and chromium it was found that in order to reduce the rate of oxidation to a low value more of the latter than of the former was required. Furthermore, in order to retain at 1,000° C. the same resistance as at 900° C. the chromium content had to be raised considerably, while the aluminium content had only to be raised slightly.

OTHER ASPECTS OF THE RELATIONS BETWEEN GASES AND SOLID METALS

Attention has been so far confined to the formation of oxide layers on metal surfaces, but this is not the only process that can occur when

solid metals are exposed to gases. In addition, they may adsorb gas on their surface from which it may diffuse into the metal and (1) remain dissolved, (2) accumulate under pressure in cavities, or (3) react with some constituent in the metal to form either another gas or a solid compound. Furthermore, the gas to which the metal is exposed may react at the surface with the basis metal or some other constituent to form another gas, and in this way the metal may be gradually vaporized or a certain constituent removed. When, e.g. molybdenum is heated in a stream of oxygen a volatile oxide is formed and the metal is gradually converted into vapour, and when steel is heated in a stream of hydrogen this gas reacts with the carbon to form a gaseous hydrocarbon, and thus carbon is removed as rapidly as it can diffuse to the surface.

If we consider the atoms in the interior of a metal we see that each atom is surrounded by neighbours in certain directions and at certain distances, and that the capacity of the atoms for combining with other atoms is completely satisfied. This condition does not exist, however, at the surface where the atoms in the outermost layer have no neighbours on one side. These atoms still retain a certain unsatisfied capacity for combining and are said to have residual affinity. If the metal is produced in a vacuum and kept in it the residual affinity persists, but whenever the metal is exposed to air or other gas it becomes covered with an adsorbed layer of gas. This adsorbed layer differs from a true compound in that only the residual affinities of the atoms are involved. For the formation of a true compound the conditions relating to the gas, metal, temperature, and pressure must be such that the gas atoms have a higher affinity for the metal atoms than these latter have for each other. Then the metal atoms are detached from their combination with each other and cannot be caused to combine with the gas atoms. This phenomenon is not restricted to the outermost layer of atoms, and consequently, when the conditions are such that a compound may form, the adsorbed layer quickly becomes a film of oxide or other compound which increases in thickness as explained in the preceding sections. Various aspects of adsorption are described in Chapter II. An important feature of this is that the gas molecules are dissociated into their constituent atoms, and these react readily with other adsorbed atoms. It is on this fact that the catalytic action of metal surfaces depends. Another important feature is that adsorption is specific, and only certain gases are adsorbed by certain metals. Thus nitrogen is not adsorbed by copper or gold at room temperature but is actively adsorbed by iron, chromium, and other metals that are capable of forming nitrides. Hydrogen is strongly adsorbed by most metals and carbon monoxide is adsorbed by iron and nickel.

From the adsorbed layer gas may diffuse into the metal, and owing to the fact that adsorption must precede diffusion the diffusion of gases into metals is also a specific phenomenon. Thus hydrogen which is adsorbed by practically all metals will diffuse into them, oxygen will

diffuse through many metals, but nitrogen will only diffuse through those with which it can form nitrides. The relations between adsorption and diffusion arise from the fact that gases in the molecular condition, i.e. H_2 , O_2 , and N_2 do not diffuse through solid metals, and diffusion only takes place when the gases are converted into the atomic state by the process of adsorption. It is sometimes stated that compound gases like CO , CO_2 , and CH_4 can diffuse through certain metals, but, according to Smithells (216) this is almost certainly untrue, and if carbon monoxide appears to diffuse through a metal the process involves dissociation of the gas into carbon and oxygen which diffuse separately. Owing to the fact that the consequences arising from the solution of gases by solid metal are sometimes most pronounced at the grain boundaries it has often been assumed that gas diffuses more readily along the grain boundaries than through the grains. This is true in some cases, but it is not true in general, and the question is discussed under 'Diffusion' in Chapter VI. Treatments which roughen the surface and thus increase its area facilitate adsorption and therefore diffusion. The rate of diffusion of hydrogen through nickel which has been roughened on the surface by repeated oxidation and reduction may be four times as fast as when the surface is polished. In the case of iron, etching the surface with acid may increase the rate of diffusion as much as ten times. Diffusion is decreased if the surface is covered with an adsorbed film which hinders the adsorption of the diffusing gas or with an oxide film which prevents access of gas to the metal surface. Thus the rate of diffusion of hydrogen through aluminium is reduced to one-tenth of its normal value by anodic oxidation.

When iron or steel is immersed in hydrochloric or sulphuric acid hydrogen is produced at the surface of the metal. This is in the atomic (nascent) condition, and although most of it bubbles off from the surface of the metal some of it diffuses into it. This diffusion of nascent hydrogen into iron can take place at atmospheric temperature, but no appreciable amount of molecular hydrogen can enter the metal at this temperature. If, however, iron is heated in molecular hydrogen the amount diffusing into the metal increases with the temperature. The operation of pickling, used to remove oxide scales from metals, involves immersion in acid, and during the process hydrogen is taken up by the metal. This sometimes results in the formation of blisters and more frequently in temporary embrittlement of the metal. The production of blisters on thin sheets during pickling is believed to be due to the diffusion of hydrogen being interrupted by inclusions. The hydrogen then tends to accumulate in the molecular form between the inclusion and the metal, and as atomic hydrogen continues to diffuse into this space, while the molecular hydrogen formed there cannot diffuse away, a high pressure which leads to a blister results. This, and pickling brittleness are further discussed in Chapter X.

A phenomenon similar to that described above is the 'gassing' of

copper. The most widely used variety of copper is that known as 'tough pitch' which contains about 0.04 per cent. of oxygen as the principal impurity. This oxygen exists in the solid metal as small particles of copper oxide mainly situated at the boundaries of the metal crystals. When such copper is heated in an atmosphere containing hydrogen this gas diffuses into the metal and combines with the oxide forming water vapour which, being a compound gas, cannot diffuse out again. Thus a high gas-pressure is developed at the crystal boundaries, and they are forced apart so that the intergranular cohesion is decreased and in some cases destroyed. This phenomenon occurs because solid copper is not capable of dissociating water vapour. With iron, on the other hand, water vapour is not formed when hydrogen diffuses into metal containing oxide, for heated iron dissociates this gas. The corrosion of aluminium is accompanied by the formation of a certain amount of nascent hydrogen, and some of this gas diffuses into the metal. The actual solubility of hydrogen is too small to measure but it is not negligible, and thus diffusion can occur. The gas which thus diffuses into the metal accumulates in existing blowholes and contraction cavities and, as explained in the next chapter, leads to trouble when aluminium previously exposed to corrosion is remelted for casting.

Besides forming oxide on the surface, oxygen can diffuse into solid metals and there form oxide either as grain boundary films or as particles in the interior of the crystals. The formation of oxide films round the grain boundaries in nickel steels has already been described in connexion with Pfeil's experiments, and Portevin, Prétet, and Jolivet observed a similar penetration of oxide in iron-aluminium alloys, although in this case the alumina appeared in the form of clusters of small particles. In general, the relations between the formation of oxide scales, grain boundary films continuous with the scale, and oxide particles within the metal and out of contact with the scale, depend on the temperature, the oxygen pressure, and the nature of the metal concerned. If the oxide forms very slowly as a result of low oxygen pressure or the nature of the metal, the most conspicuous feature is the diffusion of oxygen into the metal and the production of oxide particles. Under conditions that permit more rapid oxidation boundary films continuous with the scale tend to form, and when oxidation is still more rapid the metal is converted to oxide, layer by layer. When steel is heated at a high temperature in an oxidizing atmosphere the formation of a continuous oxide scale takes place fairly rapidly. The complete conversion of successive layers of the metal to oxide is therefore the most conspicuous feature of the process, and the formation of oxide films round grain boundaries or of particles in the grains is not so noticeable. These changes take place, however, to some extent in the layer of metal in immediate contact with the scale, and are responsible for the fact that the properties of a surface from which scale has been removed are different from those of one that has never been oxidized. If the rate

of oxidation is reduced the formation of scale becomes less important, and the other effects of oxidation more important, and these conditions may be realized by using a less oxidizable metal, by reducing the pressure or by decreasing the oxygen content of the atmosphere used. Thus penetration of oxygen into the metal is more conspicuous in alloy than in ordinary steels, and it occurs to a marked extent when pure iron is heated *in vacuo* in contact with iron oxide.

The rate of diffusion of hydrogen in heated solid metals is such that it diffuses throughout them, and unless it accumulates in contact with inclusions or reacts with some other constituent the result is the production of a solution of hydrogen in the metal. Oxygen and sulphur diffuse much more slowly, however, and their effect is confined to the layer of metal close to the surface. There the content of dissolved oxygen or sulphur is first raised to the limit of solid solubility, and then oxide or sulphide begins to separate. For this reason the surface of a metal that has been heated in an atmosphere containing oxygen or sulphur or both is different from that of the underlying metal, and is known as the sub-scale layer. Other important gas-metal phenomena are (1) the decarburization of steel, described in Chapter X, (2) the carburization and nitriding of steel, described in Chapter XIII and (3) processes described generally as 'cementation' which involve altering the composition of the outer layers of metals by causing other elements to diffuse into them.

THE PHENOMENA INVOLVED IN ELECTROCHEMICAL CORROSION

In the foregoing sections attention has been confined to a consideration of the direct combination between metals and gases, and the effect of the presence of liquids has only been mentioned incidentally. It is now necessary to consider the mechanism of corrosion when water, acids, alkalis, or salt solutions have access to the surface of the metal. This type of corrosion is mainly electrochemical and involves, in the first instance, solution of the metal. A description of its mechanism must therefore be preceded by a brief account of the relevant electrochemical phenomena and the terms used.

Electrolytes.

It has already been explained (Chapter II) that chemical combination between atoms of different elements may arise in either of two ways: (1) by the transfer of electrons from the atoms of one element to those of the other, thus leaving the first atoms with an excess of positive charges and giving the others an excess of negative charges; (2) by the sharing of electrons in such a way that from one to four electrons of each atom are held in common in the structure of both atoms. Compounds of the first type are known as electrovalent, heteropolar or simply polar. Those of the second type are characterized as covalent,

homopolar or non-polar. A large proportion of chemical compounds can be classified into these two groups without difficulty, but many are of an intermediate character. The number of electrons that can be exchanged or shared determines the valency of the atoms concerned.

The most conspicuously polar compounds are those formed between definitely metallic and definitely non-metallic elements. When an interchange of electrons takes place the electrically neutral atoms of the elements concerned become charged ions. As metallic atoms enter into combination of this kind by detaching electrons, metallic ions have a positive charge, and the non-metallic atoms which attach these electrons acquire a negative charge. Metallic ions are known as cations, and denoted thus Na^+ , Cu^+ , Fe^{++} , Fe^{+++} , while non-metallic ions are known as anions and are denoted thus Cl^- , SO_4^{--} , PO_4^{---} . The number of dots or dashes signifies the number of positive or negative charges.

Owing to the interchange of electrons between the atoms, the crystals of heteropolar compounds may be regarded as being built up of ions rather than atoms, and the cohesion of the solid depends on the electrostatic attraction between these differently charged particles. When such compounds are liquefied or dissolved in a solvent the constituent ions may remain attached together as molecules or become separated as ions. The extent to which this separation occurs depends on the nature of the compound and the solvent in which it is dissolved. Thus the molecules of water are dissociated to a small extent into H^+ and OH^- ions, whilst in liquid hydrogen-chloride free from water there is no dissociation of the molecules. If, however, hydrogen chloride is dissolved in water forming hydrochloric acid, the hydrogen chloride is extensively dissociated into H^+ and Cl^- ions.

In water or in solutions of salts, acids, and alkalis in water, continual movement of the ions and molecules is going on; ions are constantly combining to form molecules and molecules are continually breaking up into ions. In any given solution at a particular temperature there is, however, a certain equilibrium relation between the number of ions and the number of molecules. This is known as the degree of dissociation of the compound under these particular conditions. The degree of dissociation increases as the concentration of the dissolved salt, acid, or base, decreases, but the actual number of ions per cubic centimetre increases with the concentration of the solute.

Electric currents passing through metallic conductors are carried by free electrons. Currents passing through liquids are carried by ions. Liquid conductors therefore consist of those heteropolar compounds which dissociate to some extent into their constituent ions when liquefied or dissolved in water. Such liquids are known as electrolytes, and are divided into two classes: (1) the non-aqueous electrolytes, e.g. fused salts, and (2) the aqueous electrolytes which are water, and solutions in water of salts, acids, and alkalis. Owing to the fact that the molecules of water are dissociated only to a small extent into

H^+ and OH^- ions it is a very weak electrolyte. Solutions of such acids as hydrochloric, nitric, and sulphuric are, however, strong electrolytes, because of their high degree of dissociation into H^+ , Cl^- , H^+ , NO_3^- and H^+ , SO_4^{2-} ions respectively. The class of aqueous electrolytes also includes solutions of salts such as KCl , Na_2SO_4 , $CuSO_4$, &c. (which are dissociated into K^+ , Cl^- , Na^+ , SO_4^{2-} and Cu^{2+} , SO_4^{2-} ions), and solutions of alkalis such as KOH and $NaOH$ (which are dissociated into K^+ , OH^- , and Na^+ , OH^- ions). H^+ ions, which are positively charged and behave in the same way as metallic ions, are known as hydriions, and the strength of an acid depends on their concentration. Similarly, the strength of an alkali depends on the concentration of OH^- (i.e. hydroxyl) ions.

In practice, natural waters are the electrolytes involved in electrochemical corrosion. Pure water, as just mentioned, is a weak electrolyte, but natural waters contain acids, alkalis, and salts in solution and are therefore much stronger. Natural waters from different sources vary in composition to a pronounced extent, and on this account aqueous solutions containing known amounts of acid, alkali, or salt are generally used instead of water in the study of corrosion phenomena.

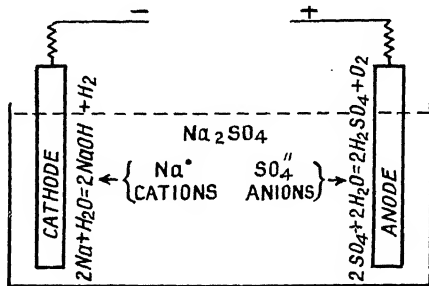


FIG. 212.

The passage of an electric current through an electrolyte involves directional movement of the ions. If, e.g., two platinum electrodes are placed in a solution of sodium sulphate and connected to the poles of a battery, positively charged Na^+ ions will move towards the electrode that is connected to the negative terminal (i.e. the cathode) and negatively charged SO_4^{2-} ions will move towards the electrode that is connected to the positive terminal (i.e. the anode). On arrival at the cathode, the Na^+ ions (cations) attach electrons and become atoms, whilst at the anode SO_4^{2-} ions (anions) give up electrons and become electrically neutral SO_4 radicles. The Na atoms appearing at the cathode react with water forming sodium hydroxide and hydrogen. The hydrogen is evolved as gas at the cathode. The sodium hydroxide accumulates at the cathode thus making this part of the solution alkaline. The SO_4 radicles appearing at the anode react with water forming sulphuric acid and oxygen. The oxygen is liberated at the anode, while the sulphuric acid accumulates there, thus making that part of the solution acid. The general scheme of the electrolysis of a solution of sodium sulphate between platinum electrodes is illustrated in Fig. 212.

If, instead of the above arrangement, copper electrodes in a solution of copper sulphate are connected to the poles of a battery, somewhat different results are obtained. As before, the metallic ions travel towards the cathode, and the negative ions towards the anode. At the

cathode the Cu^{++} ions take up electrons and become atoms, which join the metal of the cathode. At the anode the SO_4^{--} ions lose electrons and become radicles, which combine with the copper of the anode forming copper sulphate which dissolves in the solution and ionizes. The net result of the process is therefore dissolution of copper at the anode and deposition of copper at the cathode.

It follows from the foregoing that when a current passes between two electrodes immersed in an electrolyte, directional movement of the ions takes place. On arrival at the appropriate electrode the ions lose their electric charges and become atoms or radicles, and the atoms or radicles thus produced may (1) either combine with the solvent, as in the case of sodium or sulphate produced at platinum electrodes, (2) be deposited on the electrode, as in the case of copper on a copper cathode, or (3) react with the electrode, as in the case of sulphate produced at a copper anode. Other reactions which may occur at the electrodes will be described presently.

Electrode Potential.

According to the classical theory of Nernst each metal has a definite solution pressure which is a measure of the tendency of the metal to pass into aqueous solution in the form of ions. When a metal is placed in a solution of one of its salts, metal atoms therefore tend to enter the solution as ions, but at the same time ions already in the solution tend to discharge on the surface of the metal and become atoms. The solution pressure of the metal is thus opposed by the osmotic pressure of the ions in solution. Before the metal is immersed in the solution both the metal and the solution are electrically neutral, but when the number of metallic ions in the solution is altered a difference in potential is established between the metal and the solution. If the solution pressure is greater than the osmotic pressure the number of positively charged ions in the layer of electrolyte in immediate contact with the metal surface is increased, and at the solution-metal interface the solution becomes positively charged with respect to the metal. The metal therefore becomes negative with respect to the solution. If, however, the osmotic pressure is greater than the solution pressure the number of positive ions in the layer of electrolyte in immediate contact with the metal is decreased and the metal therefore becomes positive with respect to the solution.

The solution pressure of a metal is a measure of its tendency to pass into solution in the form of ions and the osmotic pressure of the ions is a measure of the tendency for the reverse change to take place. As the passage of ions into or out of solution is a basic factor in electrochemical phenomena the behaviour of the different metals is of pronounced importance. In order to study this it is necessary to ascertain the behaviour of the metals under comparable conditions, and for this purpose the potential established when a metal is immersed in a solution containing a normal concentration of its ions is measured. It is, how-

ever, impossible to measure this directly, for in order to complete the circuit two electrodes must be used. For this purpose the hydrogen electrode is used. This consists of blackened platinum saturated with hydrogen under a pressure of one atmosphere. To measure the potential between a metal electrode and a solution containing a normal concentration of its ions, the half-cell consisting of the metal immersed in this solution is connected by means of a liquid junction with a half-cell composed of the hydrogen electrode in an acid solution of normal concentration with respect to hydrogen ions. The potential difference between the metal and the hydrogen electrode is then measured and taken as the Electrode Potential of the metal.

In order to compare the different metals the potential difference between the hydrogen electrode and the acid solution is assumed to be zero and the potentiometer reading is supposed to be a measure of the potential difference between the metal and the solution containing its ions. The values for electrode potential thus obtained are therefore not absolute, but they are relative to the standard electrode and strictly comparable.

When the solution pressure of a metal exceeds the osmotic pressure of the ions in a solution containing a normal concentration of these, then the metal tends to pass into solution as ions and to assume a negative potential with respect to the solution. The greater the difference between the solution and osmotic pressures respectively the greater is the negative potential of the metal. When, however, the osmotic pressure of the ions exceeds the solution pressure of the metal the reverse change occurs. The metal tends to assume a positive potential in relation to the solution, and this potential increases with increase in the difference between the osmotic and solution pressures respectively. The values for the electrode potentials of the metals as measured against the hydrogen electrode are given in Table 48, and although the distinction between positive and negative and the actual values of the positive and negative potentials depend on the assumed zero potential of the hydrogen electrode the table shows nevertheless the order of the electrode potentials. Metals near the bottom of the table have a strong tendency to pass into solution as ions and a weak tendency to pass in the opposite direction. Metals near the top of the table have a weak tendency to pass into solution as ions and a strong tendency to pass in the opposite direction.

The values of the electrode potential given in Table 48 relate to metals immersed in solutions containing a normal concentration of their ions. The osmotic pressure of the ions decreases, however, with their concentration, and as the solution pressure may be supposed to be constant for each metal, its electrode potential clearly moves in a negative direction when the concentration of the ions in the solution is decreased. Positive potentials therefore diminish and negative potentials increase as the concentration of ions in the solution is decreased.

It is therefore possible to obtain an appreciable difference of potential between two electrodes of the same metal immersed in solutions containing different concentrations of the same salt. This is known as a concentration cell.

When a single electrode of a metal is immersed in a solution containing a normal concentration of its ions the change from the atomic to the ionic or the ionic to the atomic state proceeds until the requisite difference of potential between the metal and solution is established.

TABLE 48

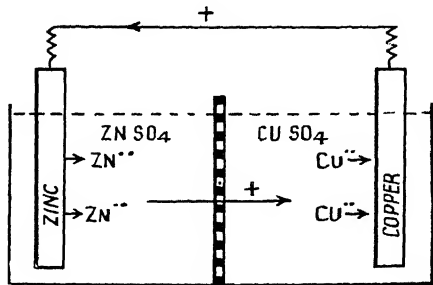
Electrode Potential of Metals in Solutions containing Normal Concentration of Ions

<i>Metal</i>	<i>Ion</i>	<i>Electrode potential</i>
Gold	Au ⁺⁺⁺	+1.36 volts
Platinum	Pt ⁺⁺⁺	+0.86 "
Silver	Ag ⁺	+0.799 "
Mercury	(Hg) ₂ ⁺	+0.798 "
Copper	Cu ⁺⁺	+0.344 "
Hydrogen	H ⁺	±0.0000 "
Lead	Pb ⁺⁺	-0.12 "
Tin	Sn ⁺⁺	-0.142 "
Nickel	Ni ⁺⁺	-0.20 "
Cobalt	Co ⁺⁺	-0.23 "
Iron	Fe ⁺⁺	-0.42 "
Cadmium	Cd ⁺⁺	-0.44 "
Chromium	Cr ⁺⁺⁺	-0.56 "
Zinc	Zn ⁺⁺	-0.77 "
Aluminium	Al ⁺⁺⁺	-1.33 "
Magnesium	Mg ⁺⁺	-1.8 "
Sodium	Na ⁺	-2.715 "
Potassium	K ⁺	-2.925 "

No further change takes place. If it is possible, however, for the charge in the solution to be continually neutralized, then the change will proceed indefinitely. This can be arranged by constructing a cell like that shown in Fig. 213. A zinc electrode is immersed in a solution of zinc sulphate and a copper electrode in a solution of copper sulphate, the two solutions being separated by a porous partition which prevents convection but allows the current to pass. When the zinc electrode is immersed in the solution it becomes negatively charged as the result of cations entering the solution, and equilibrium is established when the negative potential of the zinc is -0.77 volts. The copper becomes positively charged as a result of cations leaving the solution, and equilibrium is established when the positive potential of the copper is +0.344 volts. On open circuit therefore there is a difference in potential of 1.114 volts between the copper and the zinc, and no further change takes place. If, however, the copper and the zinc electrode are connected by a wire, the charges on the two electrodes neutralize each other and current flows in the circuit. Positive electricity passes from the zinc

to the copper through the electrolyte, and from the copper to the zinc in the wire. Thus zinc is continuously dissolved and copper is continuously deposited.

The metals at the top of the electrochemical series (Table 48) are those which are oxidized with difficulty and easily reduced. They exhibit a strong tendency to pass from the ionic to the atomic state and a weak tendency to pass in the opposite direction. These are the 'noble' metals. Those at the bottom of the electrochemical series are easily oxidized and difficult to reduce. They exhibit a weak tendency to pass from the ionic to the atomic state and a strong tendency to pass in the opposite direction. These are the 'reactive' metals. For various reasons it is most convenient to refer to the relative positions of metals in the electrochemical series in terms of nobility and reactivity. In this sense nobility does not necessarily mean that the metal in question is actually a noble metal, but only that it occupies a higher position in the series than the metal with which it is being compared.



. 213.

If one metal is immersed in a solution containing ions of another more noble metal, atoms of the reactive metal pass into the ionic state, and ions of the noble metal pass into the atomic state, i.e. the noble metal is plated on the reactive metal. Thus a given metal can usually replace from solution any metal which stands above it in the electrochemical series, e.g. a solution of silver nitrate boiled with metallic copper yields metallic silver and copper nitrate, zinc precipitates lead from a solution of lead acetate, iron replaces copper when immersed in a copper-salt solution, and so on. As the cations in water and acids are hydrogen ions the position of hydrogen in the electrochemical series is important. Metals that are more reactive than hydrogen can displace its ions from water and acids, while hydrogen can displace from simple salt solutions those metals which are more noble than it is. Both of these statements require qualification, for the displacement of hydrogen can only proceed if the atomic hydrogen can be liberated as gas or oxidized by dissolved oxygen, and the displacement of noble metals by hydrogen cannot be accomplished by the gas under ordinary pressure, but only when a catalyst such as platinum is present to promote its change into the ionic state.

Polarization and Overvoltage.

If two silver electrodes are immersed in a solution of silver nitrate some ions pass from the solution to the electrodes, and, owing to the removal of positive charges from the solution, it becomes electrically

negative with respect to both electrodes. If the solution is of normal concentration the potential of the electrodes with respect to the solution is $+0.799$ volts on the hydrogen scale. If the silver electrodes are now connected to the poles of a battery, the potential of the one connected to the negative pole will be depressed below the equilibrium value and further deposition of ions will occur, while the potential of the one connected to the positive pole will be raised, and atoms will pass into solutions as ions. Thus there is dissolution of metal at the anode, and deposition at the cathode. The current passing through the cell forces the positively charged Ag^+ cations to move towards the cathode, and the negatively charged NO_3^- anions to move towards the anode. The dissolution of silver at the anode makes the concentration of silver ions round this electrode higher than elsewhere, while the deposition of silver at the cathode makes the concentration of silver ions round this electrode lower than elsewhere. The concentration of ions at the anode tends to prevent further ions entering the solution, and the depletion of ions at the cathode tends to prevent their deposition. Thus the alterations in concentration produced by the current give rise to conditions that are unfavourable to the passage of the current. The amount of current forced through the cell by a given E.M.F. is slightly decreased. This effect is known as concentration polarization. So long as the current is forced through the cell at a slow rate the effect of polarization is small, since the local differences of concentration produced by the current will be largely destroyed through diffusion between the body of the solution and the layers next to the electrodes. Stirring the electrolyte also tends to eliminate the effects of this type of polarization.

Polarization may also be produced by accumulation of the products of electrolysis on the electrodes. Blackened platinum saturated with hydrogen forms a reversible system. It is in equilibrium with aqueous solutions at one potential only, and if this is altered hydrogen passes from the electrode into the ionic condition or from the ionic condition into the gaseous condition. On any other material than blackened platinum the production of hydrogen gas in bubbles does not occur unless the potential is depressed distinctly below the equilibrium value. Thus in a cell in which hydrogen ions are being discharged at the cathode, current does not necessarily flow whenever the potential at the cathode is depressed below the equilibrium value. Before it can flow freely the potential must be sufficient to cause the evolution of hydrogen gas as bubbles, and the difference between this and the equilibrium value is known as overpotential or overvoltage. The magnitude of this depends very greatly on the nature of the cathodic material and to a smaller extent on the character of the surface. As rough surfaces favour the formation and disengagement of bubbles, the overpotentials of such surfaces are lower than those of smooth surfaces. Table 49 taken from Evans (219) indicates the probable values of the overpotential of the commoner metals in acid liquids.

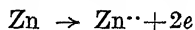
TABLE 49

Approximate Hydrogen Overpotential on Different Cathode Materials

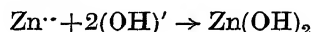
Platinum (blackened)	. very small.
Platinum (bright)	. 0.1 volt.
Gold 0.02
Silver 0.1
Nickel 0.15
Iron 0.20
Copper 0.25
Cadmium 0.5
Tin 0.5
Lead 0.6
Zinc 0.7
Mercury 0.8

Anodic Corrosion by Means of an Externally Applied Current.

In general, if two metal electrodes are immersed in an electrolyte and connected to a battery the one connected to the positive pole undergoes dissolution. So far, anodic dissolution has been described as a simple change from the atomic to the ionic state, thus

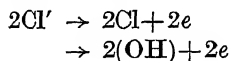


but on entering the solution the Zn^{++} (or Fe^{++}) ions combine with OH' or Cl' (or other anions) thus

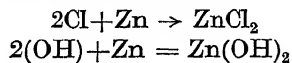


so that the final result of the dissolution of the metal is the formation of a compound which, however, may be to some extent ionized in solution.

The above changes may equally well be described as beginning with the discharge of anions on the metal surface, thus



followed by the combination of the Cl or OH with metal, thus



and then by the ionization of the compound.

Because the changes at the anode can be described in different ways it does not follow that the reactions can take place in different ways and, in general, the anodic conditions may be described as follows: Metal ions tend to enter the solution and anions tend to discharge on the metal. At the surface of the metal a compound is formed by the meeting of the ions. If this compound is insoluble it clings either loosely or tightly to the metal surface; if it is soluble it passes into solution and is ionized. If no metal ions tend to enter the solution no compound is formed, and

discharged anions will accumulate on the surface until the flow of current is interrupted or evolution of gas begins. Thus when a sodium chloride solution is electrolysed between platinum electrodes there are no platinum cations entering solution to combine with the Cl' ions, consequently these ions discharge on the surface of the anode and chlorine gas is evolved.

When a soluble compound is formed at the anode there is nothing to interfere to any extent with its continued dissolution. It is true that accumulation of the ions of the metal in the vicinity of the anode results in concentration polarization which retards the dissolution, but the effect is not very pronounced. When, however, the anions combine with the anode to form an insoluble compound on or near its surface, dissolution may be partly or completely prevented. The degree of protection afforded by such a compound depends on its physical nature. If it forms a continuous adherent film impervious to ions it effectively prevents dissolution, whereas if it only forms a loosely adherent, discontinuous, and porous coating it has little effect in retarding the attack on the underlying metal. In other words, the influence of the physical nature of the films is the same in this case as in direct oxidation.

If two or more different kinds of anions are present in the corroding solution, the course of dissolution depends on their respective properties and concentrations. If the anions present in the largest proportions form an insoluble compound with the metal of the anode, the rate of attack is likely to fall off as the protective coating is built up, but whether the attack will ultimately cease or not depends on the ability of the other anions to penetrate this film and on the type of compound formed by them. If the anions present in the largest proportions form a soluble compound the attack will be rapid at first, but it may fall off with time if the other ions form an insoluble compound. Under suitable conditions the soluble compound formed at the anode by anions of one kind is reduced at some distance from the anode by the other anions. An insoluble compound is thus formed, but as it does not adhere closely to the metal its protective action is likely to be negligible. This condition is realized when the anions that form the insoluble compound are mainly used up in reducing the soluble compound, and are thus prevented from being discharged directly on the surface of the metal. It is possible, however, for insoluble films to be formed on the surface of the anode even when the anions responsible for the formation are present in small concentrations. This is due to the cumulative effect of the discharge of anions of this kind. In the early stages of the attack the majority of the anions discharged on the metal may form a soluble compound which passes into solution. But if a few of the other anions continue to reach the surface of the metal they gradually build up a protective layer. OH' ions are very effective in this respect, and because the films formed by them are in general very insoluble and impervious, they give rise to protective films when present in quite small concentrations. Cl' anions

on the other hand are very effective in penetrating protective films and continuing the dissolution of the anode.

When the anodic dissolution of a metal is stopped or greatly retarded by the formation of a protective film it is said to have become 'passive', and when the metals that are situated below copper in the electro-potential series exhibit resistance to corrosion in water, acids, alkalis, or salt solutions it is almost invariably because of 'passivity'. Thus it may be said that, in general, resistance to electrochemical corrosion depends either on 'nobility', i.e. a weak tendency to pass into the ionic condition, or on 'passivity', i.e. a strong tendency to form protective films. Nobility is an intrinsic property of such metals as gold, platinum, and silver. Passivity depends to a large extent on the conditions to which the metal is exposed as well as on its intrinsic properties.

Because of the insolubility and impermeability of their hydroxides, most metals become passive when they are made the anode in solutions containing a high concentration of OH' ions, e.g. solutions of caustic alkali such as NaOH or KOH . It is a remarkable fact, however, that many metals become covered with a protective film of oxide or hydroxide when subjected to anodic action in a neutral or even an acid solution. Aluminium, e.g., when subjected to anodic action in a solution of sodium sulphate, or even in sulphuric acid, does not give rise to soluble aluminium sulphate, but becomes covered with a skin of oxide or hydroxide formed by the action of the OH' ions present in small amounts in the solutions. This skin tends to protect the metal, and its protective effect increases as it thickens. Raising the applied E.M.F. increases the penetrating power of the anions. Thus when aluminium is polarized in a sulphuric-acid solution the protective skin is effective while the E.M.F. is less than 25 volts. Above this value, however, the ions are able to break through the skin and a current passes comparatively freely. An interesting feature of the insulating film formed on aluminium is that it only prevents the passage of a current in one direction. Thus if the direction is reversed so that the aluminium becomes the cathode, a current flows comparatively freely. Zirconium, tantalum, niobium, and several other metals also exhibit this phenomenon.

When iron is made the anode in a solution of dilute sulphuric acid or sodium sulphate, SO_4' ions are discharged on it and soluble iron sulphate is formed. If the current density is kept low dissolution of the iron continues because only the predominant SO_4' ions are discharged on its surface. If, however, the current density is sufficiently increased OH' ions which are present in small amounts are also discharged on the anode, and a film of hydroxide is gradually built up. When a certain limiting current density is reached the current commences to diminish with time and may finally drop almost to zero unless the applied E.M.F. is high enough to promote the formation of oxygen gas at the anode. In any case, the dissolution of the iron becomes very small once the conditions are favourable to the discharge of OH' ions on its

surface, and Evans has shown that such action as does take place is confined to the water line. This is an observation of great significance and wide application. Whenever the immersed portion of a metal becomes passive as a result of the formation of a protective film, corrosion is liable to continue at the water-line. This appears to be due to the fact that films formed there tend to become detached from the surface and cling to the liquid-air interface.

If an iron anode is rendered passive in a dilute solution of acid by suitably increasing the E.M.F., it soon returns to the active state if the current is cut off. In a solution of a neutral salt, however, the passive condition persists for a longer time unless Cl^- ions are present. The presence of alkalis increases the concentration of OH^- ions, and consequently facilitates the development and maintenance of 'passivity'. Strongly oxidizing salts such as chromates also facilitate the passage of many metals into the passive condition. Chromium, nickel, and cobalt become passive under similar conditions to iron, i.e. the passage into this state is facilitated by the presence of alkali and delayed or prevented by the presence of acid. Chromium and nickel become passive more readily than iron while cobalt is less easily put into this condition. Tungsten and molybdenum form oxides of an acidic character which are freely soluble in alkalis and less soluble in acids. These metals therefore exhibit the reverse behaviour to iron, chromium, and nickel. They tend to remain active in the presence of alkali and become passive in the presence of acid. An interesting example of anodic behaviour is provided by brass. When this alloy is made the anode in a solution of sodium chloride both zinc and copper dissolve as chloride. The copper, however, is then precipitated by the zinc in the uncorroded brass, and forms a loose deposit on the surface of the anode. Thus the final effect of anodic dissolution is the removal of zinc from the alloy and the conversion of the surface of the anode into a porous layer of copper. This is called 'dezincification'.

Cathodic Action.

If two strips of different metals are immersed in a solution of an electrolyte and connected by a wire outside it, then as the potential at the surface of one metal is different from that at the other, a current will flow in the circuit. At the surface of the reactive metal anions will be discharged and will react with it. If the product is insoluble and adheres in the form of a film to the surface of the anodic metal, the current will tend to decrease. If, however, it is soluble, dissolution of the anode will continue. In order to describe the cathodic reactions attention will be confined to conditions that permit continuous dissolution at the anode.

At the surface of the more noble metal cations will be discharged. If the electrolyte is a salt of a heavy metal the discharged cations may be deposited on the surface of the cathode metal. If, however, the

electrolyte is water, or a solution in water of an acid, an alkali, or a salt of a light metal (e.g. Na_2SO_4 , KCl , CaCl_2) then H^+ ions will be discharged on the surface of the cathode metal. In the case of water, acid, or alkali they are discharged directly because they are the only cations present, but in the case of a salt solution they are produced indirectly. In the first place Na^+ , K^+ , Ca^{++} , or Mg^{++} ions are discharged, but these then combine with water forming hydroxide, and hydrogen ions are discharged on the cathode. As solutions of salts of heavy metals are not important in corrosion it may be said that, in general, whether the electrolyte is water or a solution of an acid, a salt, or an alkali, H^+ ions are discharged on the cathode. Furthermore, if the electrolyte is a solution of a salt of one of the light metals (Li , Na , K , Mg , Ca , Ba) an alkaline hydroxide tends to accumulate at the cathode.

As soon as hydrogen begins to accumulate on the more noble metal the potential will be altered in such a way as to reduce the E.M.F. of the cell, and if this accumulation continues, the potential at the noble electrode will become equal to that at the reactive electrode, and dissolution of the anodic metal will stop. If, however, before that state is reached, the noble electrode becomes so saturated with hydrogen that the gas begins to stream away as bubbles, then some current will continue to flow and dissolution of the anode will proceed. If the solution does not contain anions capable of forming a passive film on the anode, the evolution of hydrogen in bubbles will depend on (1) the electrode potential of the two metals, (2) the hydron concentration of the solution, and (3) the overpotential value of the noble metal.

If the difference in potential between the two metals is not sufficient to promote the evolution of hydrogen gas at the cathode, dissolution of the anode will stop unless hydrogen is removed from the cathode in some other way. This can be effected by oxidation, and if the solution contains dissolved oxygen, dissolution of the anode will proceed at a rate that is determined by the amount of oxygen available for combination with hydrogen at the cathode. Since the solubility of oxygen in water is low, the current produced by oxidation of hydrogen at the cathode is in general small, and the dissolution of the anode is therefore slow. Nevertheless, this is a very important phenomenon in corrosion.

In order that current may continue to flow between a more reactive and a less reactive metal the conditions must be such that no insoluble film is formed on the anodic metal, and at the cathodic metal hydrogen must either be evolved as bubbles or be oxidized by dissolved oxygen or some other agent. If no current flows, no electrochemical corrosion takes place. Consequently, corrosion may be said to depend on the evolution of hydrogen from the cathode or on the diffusion of oxygen to it. Thus Evans (219), who has been largely responsible for developing the ideas that now prevail on the effect of oxygen, and on whose work much of this section has been based, recognizes two types of electro-

chemical corrosion, namely the Hydrogen-Evolution Type and the Oxygen-Diffusion Type. Corrosion may be due to either of these processes acting alone, or it may involve the combination of both.

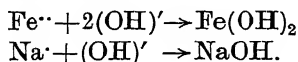
GENERAL FEATURES OF ELECTROCHEMICAL CORROSION

The electrochemical phenomena on which corrosion depends have been considered briefly in the foregoing sections, and it is now necessary to explain how the various factors described combine to produce corrosion. It has been shown that anodic dissolution takes place when a metal is immersed in an electrolyte and connected to the positive pole of a battery the negative pole of which is connected to another electrode also immersed in the electrolyte. If the battery is omitted from the circuit, and the two electrodes are connected by a wire, anodic dissolution takes place in much the same way provided that one of the metals is more noble than the other. Under these conditions the more noble metal functions as a cathode, and the reactions described in the previous section occur at its surface. Conditions under which metals are subjected to an external E.M.F. are rarely realized in practice except when they are exposed to the action of stray electric currents such as occur in the ground in the vicinity of electric transport routes. Conditions under which dissimilar metals in contact are immersed in an electrolyte are more common, and the rapid dissolution of the more reactive metal which then takes place is comparatively easy to explain. The general case of corrosion is, however, that of a single metal in contact with an electrolyte, and it is the conditions then realized that have to be explained. The anodes and cathodes which take part in the electrochemical process are different points on the surface of the same metal, and as these points may be close together reactions between anodic and cathodic products readily occur. Furthermore, the products of the cathodic reaction may influence the conditions at the anodes.

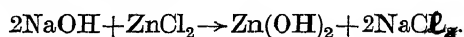
In considering the general features of electrochemical corrosion it is worth while to repeat briefly what has already been said about the type of electrolytes with which we are concerned, the metals that undergo electrochemical corrosion, and the reactions that occur at anodes and cathodes. The basic electrolyte is pure water which contains H^+ and OH^- ions. Natural waters, and solutions prepared for the study of corrosion contain dissolved salts such as sodium chloride, &c., which give rise to Na^+ and Cl^- ions, and if the solution is acidic the concentration of H^+ ions is increased relative to that of OH^- ions, while if it is alkaline the concentration of OH^- ions is increased relative to that of H^+ ions. In general, therefore, the electrolytes concerned contain H^+ , Na^+ , and other light metal cations and OH^- , Cl^- , and the other anions. The metals that undergo electrochemical corrosion are those that have negative electrode potentials, i.e. lie below hydrogen in the electrochemical series (Table 48). The order from most noble to most reactive

is Pb, Sn, Ni, Co, Fe, Cd, Cr, Zn, Al, Mg, Na, K, but the behaviour of the metals is also influenced by their overpotentials (Table 49) and the readiness with which they become passive. Pb, Sn, Ni, Cr, and Al are easily passivated. When freshly cleaned by abrasion and immersed in an electrolyte, corrosion frequently comes to a standstill as a result of the building-up of a protective film of hydroxide. Iron and zinc are not so readily passivated, and although the difference in this respect between these metals and those just mentioned is one of degree and not of kind, the fact remains that iron and zinc continue to corrode under conditions which lead to the passivation of the other common metals. As the practical importance of the corrosion of iron exceeds in importance that of all other metals most of the studies of corrosion have been concerned with it, and the interest shown in the corrosion of zinc is mainly based on the fact that its behaviour is in many respects similar to that of iron.

When iron or zinc is immersed in an electrolyte of the type described above the following reactions can occur. At anodes, metal ions combine with OH' ions or Cl' ions to form hydroxide or chloride. As hydroxide tends to be insoluble, its formation tends to lead to the cessation of anodic action. It is the readiness with which insoluble hydroxide films are formed on chromium, nickel, and aluminium that distinguishes them from iron and zinc on which protective films are only formed under favourable conditions, i.e. when there is a good supply of OH' ions. As chloride is soluble its formation leads to the continuance of anodic action. At cathodes, H' ions discharged on the surface may be evolved as gas or combine with dissolved oxygen to form water. These primary cathodic reactions are, however, accompanied by others that have an important bearing on corrosion. If the electrolyte contains only H' and OH' ions these primary reactions are the only ones that occur, but if other metallic ions are present originally, or appreciable amounts of the corroding metal have entered solution, then the discharge of H' ions on the metal is accompanied by reactions between the other cations (Fe⁺⁺, Zn⁺⁺, Na⁺, &c.) and OH' ions to form hydroxide, thus



H' ions are then discharged on the metal, Fe(OH)₂ tends to adhere to the cathode while NaOH passes into solution and increases the number of OH' ions in the electrolyte. Finally, NaOH formed at the cathodes may react with metallic chloride formed at the anodes to form metal hydroxide and sodium chloride, thus



Hydroxide formed by the discharge of OH' ions at anodes or by the combination of metal ions and OH' at cathodes tends to inhibit further action, but hydroxide formed by the combination of anodic and cathodic products does not have this effect except under special conditions.

In considering one metal in contact with an electrolyte the question immediately arises, What distinguishes anodes from cathodes? and three cases may be distinguished. In the first place, the anodic and cathodic points or areas may be determined by some intrinsic characteristics of the metal, i.e. some points or areas are more reactive and thus become anodes while the others become cathodes by difference. Secondly, the anodic and cathodic points or areas may be determined by some characteristic of the environment, i.e. the external conditions prevailing at one part of the metal may promote cathodic reactions while those prevailing at others may promote anodic reactions. Finally, the anodic points or areas may not be determined by any intrinsic characteristics of the metal or environment as such, but by the changes

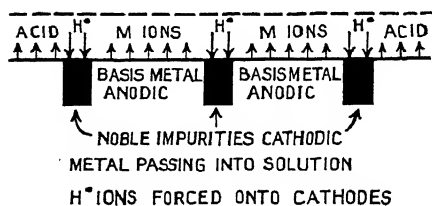


FIG. 214.

that take place at the metal surface when it comes into contact with the environment. The conditions that lead to the differentiation of anodic and cathodic areas are of great importance in connexion with corrosion, for if no such differentiation occurs there is no corrosion, and when it does

occur the distribution of anodes and cathodes determines the distribution of corrosion, which is one of its most important aspects, the other being the rate of corrosion. The three cases mentioned above may therefore be considered, giving attention first to the conditions that arise when there is a clear differentiation between reactive and noble areas in the metal, and then to those that arise when the differentiation is due to the environment or the reactions of the metal to the environment.

Corrosion Due to Areas of Different Reactivity on the Surface of the Metal.

The simplest example of this type of corrosion is provided by a reactive metal with isolated noble impurities. This case is illustrated in Fig. 214. The dominant reactive metal becomes the anode, and its ions enter the solution. At the same time hydrogen ions are discharged on the noble impurities which constitute the cathodes. If the difference in potential is great enough to promote the evolution of hydrogen gas from the cathodes, or if oxygen is available for combining with hydrogen at the cathodes, corrosion of the reactive metal will proceed. If not, despite the presence of the electrolyte and the difference in potential between different parts of the metal, no corrosion will take place. All metals which contain two or more constituents behave to some extent in the manner described above. Consequently, the corrosion of a pure metal is increased by the addition of elements that lead to the appearance of a new constituent. If this is more noble than the basis metal its presence in the alloy will promote the corrosion of the basis metal,

but the extent to which this takes place depends on its overpotential. If, however, the new constituent is less noble than the basis metal it will become anodic and suffer corrosion instead. In the early stages of corrosion only a small quantity of a noble impurity may be exposed at the surface, but as corrosion proceeds more and more of this constituent will be exposed as a result of the removal of the basis (reactive) metal. Thus the rate of corrosion will tend to increase with time. The initial stage of relatively slow corrosion is known as the Period of Induction.

Many alloys and commercial metals have a duplex structure and behave to some extent in the manner described above. Zinc is a highly reactive metal with a high overpotential. When pure zinc is immersed in acid it liberates hydrogen very slowly, because the cathodes have to be provided by certain areas in the zinc. The presence of nobler impurities of low overpotential, e.g. iron and copper, greatly accelerate the corrosion, while nobler impurities of high overpotential, e.g. lead and mercury actually diminish the rate of attack. High-grade commercial zinc contains 99.95 per cent. of this metal. By fractional distillation chemically pure zinc of 99.99 per cent. purity is regularly produced, and some of this zinc is spectroscopically pure. Dissolution tests in 10 per cent. hydrochloric acid have shown that in the time required for commercial zinc to be completely dissolved the chemically pure zinc lost 53 per cent. by weight, whilst the spectroscopically pure metal lost only 0.02 per cent. In the case of iron, which has a low overpotential value, the reaction with acids is less dependent on the presence of impurities than with zinc. Even electrolytic iron causes quite a brisk liberation of hydrogen from hydrochloric acid. Nevertheless the velocity of corrosion of iron by acids is increased by the presence of other constituents. With aluminium also the rate of attack is accelerated by such means, but in this case the effect may be due to the impurities causing discontinuities in the oxide film rather than to the provision of cathodic areas. In duplex alloys such as $\alpha\beta$ -brass, anodic and cathodic areas are provided by the constituents in the alloy. In this case the α functions as the cathode and the β as the anode.

When the other elements present in a basis metal form a solid solution instead of giving rise to new phases the conditions that arise are quite different from those described above. In this case if the added metal is more noble or becomes passive more readily it will retard corrosion of the basis metal. Thus noble metals such as gold, silver or copper will, in general, increase the resistance to corrosion of more reactive metals with which they form solid solutions, and metals such as chromium, aluminium, and nickel which readily become passive have a similar effect. When corrosion of solid solutions consisting of two metals of different potential does take place the more noble metal is liable to be redeposited as in the 'dezincification' of brass. As the redeposited copper forms a porous rather than a protective layer it

serves to accelerate the attack on the alloy by providing cathodic areas. In such cases the rate of corrosion tends to increase as it proceeds.

In the search for industrial corrosion-resisting alloys the greatest success has been achieved by the addition of metals that readily become passive, and the importance of the homogeneous distribution of these metals throughout the alloy is demonstrated by the behaviour of stainless steel in certain conditions. The steel concerned is rendered resistant to corrosion by the addition of about 18 per cent. of chromium and 8 per cent. of nickel, and the composition is such that moderately rapid cooling retains it in the austenitic condition at atmospheric temperature, i.e. the chromium, nickel, and carbon are dissolved in solid solution in γ -iron. Homogeneous austenite is not the stable phase in this steel at temperatures below about $800^{\circ}\text{C}.$, but it can be retained down to atmospheric temperature by moderately rapid cooling and then persists so long as the metal is not severely deformed. If, however, the steel is heated in the range of $500\text{--}700^{\circ}\text{C}.$ carbide separates from solution at the boundaries of the austenite grains. This carbide contains a high proportion of chromium, and as the rate of diffusion of this metal is much slower than that of carbon the carbide tends to be made up of carbon drawn from all over the grains and of chromium drawn from near the boundaries. The mechanism of this change, the constitutional conditions on which it depends and the circumstances under which it takes place in the above manner are fully considered in Chapter XII. Here all that need be said is that certain treatments produce conditions under which the chromium content of the austenite grains is high, while near the grain boundaries it is low. On exposure to the atmosphere or immersion in an electrolyte, protective films are readily formed over the greater part of the surface of the steel, but over narrow strips round the crystal boundaries no such films are formed. When in contact with an electrolyte the areas covered by protective films become cathodic to the unprotected regions round the crystal boundaries, and as the cathodic surface is large relative to the anodic, rapid dissolution takes place at the boundaries. In a very short time the steel attains a condition in which the grains are separated from each other by corrosion, and the metal practically disintegrates.

The intercrystalline corrosion of austenitic stainless steel is a very good example of the differentiation of anodic and cathodic areas resulting from the formation of protective films on certain parts of a metal and not on others. It will be seen later that the distribution of anodes and cathodes is generally due to the formation of films, but in most cases the conditions that determine the positions of the films are characteristic of the electrolyte or the reaction of the metal to the electrolyte and not of the metal as in the case above described. Films or oxide layers formed on exposure to air before immersion in an electrolyte may, however, be regarded as characteristic of the metal. Air-formed films may completely protect a metal against electrochemical corrosion,

but this usually occurs when the conditions permit repair of the film when in the electrolyte. If such repair does not take place and the oxide skin formed before immersion is cracked, discontinuous, or porous, then it may stimulate corrosion by providing cathodic areas where the oxide exists and anodic areas where it is cracked or non-existent. Air-formed oxide films may, under those conditions, serve to localize corrosion, and in many cases the anodic points are situated at discontinuities in films. Similar effects may be produced by the thicker oxide scales formed during heat treatment or rolling. These are never free from cracks which become anodic points, and frequently they are completely detached in places which thus become anodic areas. In general, the best resistance to corrosion is obtained when the scale is completely removed, the resistance is less when the whole surface is covered by scale and still less when it is only partly covered by scale.

In addition to the presence of constituents of different electrode potential, the non-uniform distribution of a passivating addition and discontinuities in previously formed oxide films, the distribution of anodic and cathodic areas may be influenced by non-metallic inclusions and the nature of the surface produced by machining or polishing. The influence of inclusions in steel has been studied by Homer (221). He found, in the first place, that the effect of inclusions in localizing corrosion was only observable when the metal had a highly polished surface and was immersed in mildly corrosive liquids. With rougher surfaces any localization of corrosion that occurred corresponded to surface markings, and with stronger corrosive liquids no localization of the attack was observed. Under appropriate conditions, however, anodic action was found to begin round inclusions of sulphides or embedded scale while silicate and alumina inclusions had no effect. Experiments showed that, in general, anodic action began round suitable inclusions while the rest of the surface was cathodic, then the anodic area extended and the cathodic areas contracted until corrosion was general. When the experiments were so conducted that no oxide film could form on the metal before immersion, every sulphide and slag inclusion became a centre of corrosion, but when an oxide film was allowed to form the number of inclusions that became active centres decreased as the thickness of the film increased. It appears that inclusions do not exert an influence by acting as cathodes but by causing discontinuities in protective films formed in the electrolyte or before immersion. In mildly corrosive liquids corrosion begins at these discontinuities and spreads by undermining the films. In strongly corrosive liquids containing high concentrations of Cl^- or SO_4^{2-} ions these penetrate the weakly protective film all over the surface, and the inclusions do not exert any localizing effect. As the early stages of corrosion of highly polished metal in mildly corrosive media are not of great practical significance it appears that the influence of inclusions on corrosion is much less pronounced than it has sometimes been supposed to be.

The effect of surface condition arises from the fact that any surface irregularities such as tool marks or accidental scratches lead to an increase in the activity of the surface. It is well known that metals exhibit their greatest resistance to corrosion when highly polished and that the resistance decreases up to a point as the surface finish becomes rougher. This is evidently due to the fact that on burrs, ragged edges, cut edges, tool marks, the edges of cracks, &c., protective films are not readily formed, and such irregularities therefore tend to localize corrosion. Crystal boundaries also tend to provide active centres, but this usually depends on the fact that small quantities of impurities concentrate there. Thus with zinc containing 0.01 per cent. of impurities anodic attack is, in the first instance, localized at the crystal boundaries, whereas with spectroscopically pure zinc the active centres are distributed evenly over the whole surface. In addition to the above, the initial differentiation of anodic and cathodic regions may arise from differences in the orientation of the crystals and from variations in the degree of internal stress existing at different points, but the effects arising from these factors are neither pronounced nor persistent.

The Effect of Variations in the Environment and the Reaction of the Metal to the Environment.

The influence on corrosion of the intrinsic characteristics of the metal has not been considered as fully as it might be, because, with the exception of a few special examples like the intercrystalline corrosion of stainless steel, it is not so important as the factors now to be discussed. It is true that the resistance of a metal to corrosion is primarily determined by its nature, e.g. zinc and iron corrode readily while aluminium, chromium, nickel, lead, tin, and copper do not, and the resistance of an alloy is determined by its composition, e.g. impurities accelerate the corrosion of zinc, whereas chromium, nickel, and aluminium retard the corrosion of iron, but for the time being we are mainly concerned with the factors that lead to the differentiation of anodic and cathodic areas and not with corrosion generally.

A metal in contact with an electrolyte may be completely immersed, partially immersed, covered with a film due to condensation or exposure to rain, or partly covered with isolated drops of electrolyte. When only parts of the surface are in contact with the electrolyte any corrosion will clearly be confined to these, but when the whole surface is in contact there are three alternatives, i.e. there may be no corrosion, localized corrosion, or general corrosion. If one of the reactive metals undergoes no corrosion when immersed in an electrolyte it means that a protective film is formed over the whole surface, and although films previously formed in air will contribute to this protection they are not usually effective unless the electrochemical conditions favour the formation of such films. If general corrosion occurs it means that films previously formed are not protective and that none are formed in the

electrolyte. If localized corrosion occurs it means that the films formed in the air or in the electrolyte are capable of partially protecting the metal, and from this point of view localized corrosion of completely immersed specimens (not in contact with other substances and not possessing characteristics that promote localization) indicates conditions intermediate between those that produce no corrosion and those that produce general corrosion. From a practical point of view, however, localized corrosion is usually more serious than general corrosion, for the total amount of metal affected depends to a pronounced extent on the quantity of oxygen reaching the surface of the metal, and the amount of corrosion is therefore the same whether the attack is localized or widespread. A given amount of corrosion concentrated at a few points causes much more rapid deterioration than the same amount spread over the whole surface, and consequently when steps are taken to retard corrosion they sometimes increase its effects unless they prevent it altogether.

The study of the distribution of corrosion is complicated by the fact that it does not remain unchanged. It may start at a large number of points and spread until it becomes general, or it may stop at most of these points and continue at a few only. Sometimes this localized corrosion once established persists indefinitely, but under other conditions it spreads and becomes general. The study is further complicated by the fact that there are no standardized tests comparable with those used in the investigation of mechanical properties, and every result obtained depends to some extent on the conditions under which it is obtained. It is true that the results obtained in a tensile test depend on the conditions under which it is carried out and have a significance different from those obtained in a notched-bar or endurance test. But the relations between one mechanical test and another, and between the results of these tests and behaviour in service, are fairly well understood, whereas no similar claim may be made for corrosion tests. Thus one experimenter may carry out an investigation under one set of conditions and arrive at conclusions that have no bearing on another set of conditions, and even when the tests involved are actual service tests a change in some factor not taken into account may completely upset the relations between different series of experiments.

In general, it may be said that no corrosion occurs on metals or parts of metals on which protective films are formed under the conditions of exposure, but that it occurs on metals and parts of metals on which no protective films are formed. It may also be said that when no corrosion occurs the explanation is evident, but the conditions that lead to the localization of corrosion and the relations between localized and general corrosion are much more difficult to understand. Before considering these it is worth while to expand what has already been said about the two types of corrosion, i.e. the hydrogen-evolution type and the oxygen-depolarization type.

Blackened platinum saturated with hydrogen is a reversible electrode, i.e. the overpotential is negligible. The electrode potential of such an electrode against a solution containing a normal concentration of hydrogen ions is zero, but as the potential of all electrodes is moved in a negative direction by decreasing the concentration of the ions, the hydrogen electrode has a negative potential in solutions containing less than the normal concentration of hydrions. Thus the electrode potential of hydrogen in neutral water is -0.406 volts.

If a cell consisting of a metal electrode and a hydrogen electrode immersed in a dilute solution of acid is made up, hydrogen gas will be evolved at the hydrogen electrode if the electrode potential of the metal is more negative than that of the hydrogen electrode. In other words when the overpotential of the cathode is negligible, hydrogen gas is evolved if the pressure of the metal ions is greater than that of the hydrogen ions entering the solution. Metal ions are forced into the solution and hydrogen ions are forced out. It follows from this that, in general, the metals situated below hydrogen in the electrochemical series (Table 48) will cause the evolution of this gas when electrodes of these metals are immersed in acid solutions and connected to a hydrogen electrode. Those metals which are situated far below it in the electrochemical series (e.g. zinc, cadmium, and iron) produce fairly rapid evolution of this gas, while in the case of those metals that are situated just below it (e.g. lead, tin, and nickel) the liberation of gas proceeds at a very slow rate. The metals which are situated above hydrogen do not cause liberation of gas in bubble form except under very special conditions.

In cases of corrosion, however, the cathodes are not hydrogen electrodes but certain points on the surface of the metal, and the overpotential of these cannot be neglected. Under such conditions the evolution of hydrogen does not take place unless the difference in electrode potential between anodic and cathodic points is greater than the overpotential of the cathodic points. Thus, although zinc is a very reactive metal, the pure metal liberates hydrogen very slowly from acid solutions because of the high overpotential of the cathodes, and the rate of solubility in acid is greatly increased by the presence of impurities of low overpotential. Owing to the lower overpotential of iron its dissolution in acids is not so dependent on the presence of impurities.

The foregoing paragraphs refer to the liberation of hydrogen gas from acids. Many of the metals standing at the negative end of the electrochemical series can, however, expel this gas from neutral and even alkaline solutions. Since the potential of hydrogen towards a neutral solution is -0.406 volts, this will clearly only be possible in the case of the most reactive metals, and then only when no film of insoluble hydroxide is formed on the anodic areas. Sodium and potassium fulfil these conditions and consequently expel hydrogen from water with

great violence. Aluminium and magnesium are also highly reactive, but they form insoluble hydroxides, and unless the conditions preclude the formation of adherent films on the anodic areas they do not liberate hydrogen from water. Iron hydroxide is appreciably soluble in water, but this solubility is decreased by the presence of alkali. Almost any natural water is capable of acting slowly on iron even in the absence of oxygen. Hydrogen gas is liberated in small quantities. As ferrous hydroxide is slightly alkaline, the rate of corrosion in stagnant water tends to decrease as this salt accumulates in solution. The decrease in the rate of attack due to this cause does not occur if the water contains a weak acid like carbon dioxide or if it is constantly changing.

Since most metals have hydroxides that are insoluble in alkalis the liberation of hydrogen from an alkali is a somewhat exceptional phenomenon. Nevertheless zinc and iron exhibit this behaviour. The ease with which zinc expels hydrogen from an alkaline solution appears to be connected with the fact that a soluble zincate (e.g. Na_2ZnO_2) and not a hydroxide is formed. The behaviour of iron is accounted for in a similar way. At fairly low temperatures and low concentrations, alkalis render iron passive, but at higher temperatures and concentrations hydrogen is liberated from the alkalis. The reaction depends on the formation of soluble complex salts (e.g. Na_2FeO_2), and can proceed indefinitely with evolution of hydrogen. This behaviour of iron and steel has an important connexion with the embrittling of boilers fed with alkaline water and of autoclaves in which reactions with hot concentrated alkalis are carried out. To some extent this embrittlement is due to the atomic hydrogen that is liberated being adsorbed by the metal, but other factors also contribute.

In most cases of corrosion the electrolyte is a natural water, and the conditions with respect to H^+ ion concentration, difference in potential between anodes and cathodes, and overpotential of cathodes, do not permit the rapid evolution of hydrogen. The progress of corrosion then depends on the hydrogen gas that accumulates at the cathodes combining with oxygen, i.e. on oxygen depolarization. This in turn depends on the presence of oxygen in the electrolyte, and although all waters and other electrolytes contain small amounts of dissolved oxygen this is soon used up, and appreciable corrosion only takes place as oxygen is conveyed by diffusion and convection from the surface of the electrolyte to the surface of the metal. As this is affected by numerous factors such as the depth of immersion of the metal, differences in depth of immersion of different parts, area of contact between the surface of the electrolyte and the atmosphere, and convection currents, the rate and distribution of corrosion depend in practice on many conditions other than those already discussed. It is this more than anything else that complicates the consideration of the effect of environment and the reaction of the metal to the environment. Thus in studying the corrosion

of a given metal in a given electrolyte the following factors have, as stated by Bengough (222), to be taken into account:

1. Preparation of the surface.
2. Method of suspension.
3. Size and shape of specimen.
4. Depth of immersion.
5. Cross-section of vessel.
6. Volume of corroding liquid.
7. Stability of apparatus.
8. Temperature and particularly its fluctuations.
9. Pressure, particularly partial pressure of oxygen and its fluctuations.

These factors have to be taken into account in studying one metal in one environment, but when corrosion is considered generally the following have also to be included:

Relating to the Metal.

1. The Electrode Potential.
2. The Hydrogen Overpotential.
3. Elements in Solid Solution.
4. Presence of different constituents.
5. Chemical reactivity.

Relating to the Environment.

1. The concentration and specific nature of the ions present in the solution, e.g. H^+ , Na^+ , K^+ , OH^- , Cl^- , SO_4^{2-} ions, and the variation of this with time.
2. The nature and distribution of surface films and corrosion products, and the variation of this with time.
3. The electrical conductivity of the solution.

The corrosion of zinc, iron, and steel in comparatively pure fresh water depends only on oxygen depolarization, but when these metals corrode in sea water or salt solutions both hydrogen evolution and oxygen depolarization are involved. It would appear that in so far as hydrogen-evolution corrosion is concerned it should be independent of oxygen supply, but experiments by Bengough and Wormwell (223) show that this is not the case. A mild-steel specimen was immersed in ammonium chloride solution over which an atmosphere of purified argon was maintained, and the rate of hydrogen evolution was determined for 65 days. This rate was initially quite rapid, but it decreased with time so that the corrosion-time curve was of parabolic type, and the rate of evolution of hydrogen at the end of the 65 days was very slow. At this stage the argon was replaced by oxygen, and besides starting oxygen-depolarization corrosion, this change had the effect of greatly accelerating the hydrogen-evolution corrosion. The hydrogen

evolution-time curve now became linear and as much hydrogen was evolved in four days under oxygen as in 65 days under argon. This indicates that oxygen has some other effect besides promoting depolarization at the cathodes, and Bengough and Wormwell attribute its action to oxidation of the film produced at anodes. In the absence of oxygen a film of ferrous hydroxide impervious to ions is formed at anodes, and it is the building-up of this film that decreases the rate of hydrogen evolution in the absence of oxygen. Complete oxidation of this film in the presence of relatively high alkalinity, at smooth or slightly attacked surfaces, gives a uniform protective layer of ferric oxide, but partial oxidation, in neutral or slightly alkaline solutions, at a surface roughened by corrosion or other means, appears to result in a pervious, heterogeneous film which allows corrosion to proceed. In this way the presence of oxygen increases the rate of hydrogen evolution from iron and steel. With zinc, however, oxygen is not required at the anode because the hydroxide formed does not prevent the entry of zinc into solution in the presence of Cl^- ions.

FILM CONTROL OF CORROSION DISTRIBUTION

It will be evident from what has been said in previous sections that when one of the reactive metals is in contact with an electrolyte there is no corrosion on surfaces or parts of surfaces on which protective films are formed, and general corrosion on surfaces or parts of surfaces on which no such films are formed. Furthermore, when protective films are formed on parts of surfaces these may act as cathodes to parts where none are formed. The consideration of the effect on the distribution of corrosion of variations in the environment and in the reaction of the metal to the environment therefore amounts to the same thing as consideration of the effect of these factors on the distribution of protective films. Except in such special cases as when lead is protected by a film of sulphate the protective films are hydroxides formed by the combination of OH^- ions with metallic ions at the surface of the metal, and while in some cases these films may be definite layers of hydroxide, in others they are simply layers of OH^- ions clinging temporarily to the surface.

We have seen that oxide films formed in air before immersion in a corrosive solution exert a certain protective influence, but unless the reaction of the metal to the solution is such that films may form during immersion, corrosion will begin at discontinuities in the air-formed film and spread by undermining it. For the present purpose air-formed films may therefore be neglected and attention confined to what happens in the electrolyte. If one of the reactive metals is cleaned by abrasion and immersed in water or a salt solution, metal ions tend to pass into the solution which thus becomes positively charged with respect to the metal. When the charge attains a certain value a condition of equilibrium tends to be reached under which, although there is

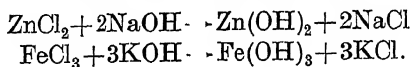
a constant interchange of ions between the metal and the solution, there is always a certain number of ions in the solution. But in maintaining equilibrium the discharge of hydrogen ions on the metal surface has the same effect as the discharge of metal ions, and amongst the ions returning to the surface a certain number of hydrogen ions will be included. If the hydrogen ions thus discharged are removed from the metal surface as gas or by combining with oxygen to form water, metal ions will continue to enter the solution in place of the hydrogen ions leaving it. The entrance of metal ions into solution is the anodic reaction and the discharge of hydrogen ions is the cathodic reaction, and it is possible for the two reactions to go on simultaneously over the whole surface, the points at which metal ions are entering the solution being temporarily distinguished from those at which hydrogen ions are leaving. But there is no need to suppose that the initial differentiation between anodic and cathodic points is determined solely by chance, for there are certain to be some intrinsic variations in reactivity between different points on the metal surface, e.g. between differently oriented crystals, between the interior of crystals and their boundaries, or between the crests and troughs of tool marks, &c. Even the slightest difference between one point and another will be sufficient to ensure that at one point the pressure of metal ions entering solution will be greater than at the other, and therefore hydrogen ions will be forced out of solution at the other point and electrochemical action will proceed.

It follows from the above that in the initial stage corrosion is more or less general over the whole surface, and the anodic and cathodic points are continually changing except in so far as there are intrinsic differences between different points on the surface. If these are considerable they will control the future distribution of corrosion, but in general they do not, and this control is exercised by differences in the environment or differences arising at the metal surface after corrosion has commenced. Once metal ions are passing into solution at some points and hydrogen ions passing out at others, anodic and cathodic points are differentiated, and current flows between them. This current is carried by metal and hydrogen ions and also by OH' , Cl' , and Na' ions. Of these the OH' and Cl' travel to the anodic points while the Na' travel with H' and metal ions to the cathodic points. There the discharged Na' and metal ions react with water to form hydroxides, and more H' ions discharge on the metal surface. The NaOH passes into solution but the metal hydroxide tends to cling to the metal surface. The formation of hydroxide at anodic and cathodic points tends to produce protective films, and the formation of NaOH tends to increase the number of OH' ions available for discharge on anodic points. The future distribution of corrosion depends on the extent to which protective hydroxide films are formed and the places where they are formed.

The extent to which protective films are formed varies with the metal and the solution. They are formed readily on chromium, aluminium, and nickel, but not on iron or zinc. Furthermore, they are formed readily in solutions containing high concentration of OH' ions, less readily in solutions in which Cl' ions predominate, and still less readily in solutions in which H' ions predominate. When there is no corrosion or when general corrosion occurs, it means that the reaction of the metal to the solution is such that a protective film is formed over the whole surface or is not formed at all, and in the latter case the cathodic points are simply points at which H' ions are temporarily being discharged. When, however, corrosion is localized it may mean either that there is some definite and persistent differentiation of the metal surface into more reactive and less reactive areas, that there is some variation in conditions at different points in the environment, or that protective films at some points can only be maintained when there is anodic dissolution at others. This latter condition is realized with iron and zinc in certain solutions. The supply of OH' ions for the formation of protective films depends on the formation of NaOH at cathodes, and the production of this depends on the continuation of electrochemical action, and consequently the whole surface cannot be protected. The factors that control the distribution of anodic and cathodic areas under different conditions of immersion in different solutions have been the subject of many investigations, and there are certain differences of opinion as to the nature of the controlling factor in different cases. In order to give an adequate account of the evidence on which these different opinions are based it would be necessary to describe in detail a large number of experiments and explain the conclusions drawn from them. This method of dealing with a subject has not been adopted elsewhere in this book, the principal object of which is to describe the general ideas that have emerged from the work on different subjects rather than to give details about particular investigations or experiments. For this reason the different views which attribute the distribution of protected areas to that of dissolved oxygen and alkali respectively will be given a brief consideration only. The former is dealt with because it was for many years generally accepted and is still widely accepted. The latter is dealt with because many experiments on which it is based cannot be explained by the older theory.

Before giving an account of the two above-mentioned theories it is necessary, however, to say something about secondary corrosion products which under certain conditions influence the progress of corrosion. We have seen that when an insoluble primary product is formed at the anodes it tends to inhibit corrosion, whereas when a soluble primary product is formed corrosion proceeds without interruption in so far as the anodes are concerned. As a rule, however, when soluble primary products are formed they are converted by secondary reactions into insoluble products the distribution of which

varies with the conditions of their formation. Secondary corrosion products are, in general, formed by reaction between the soluble anodic product and alkali formed at the cathodes, thus



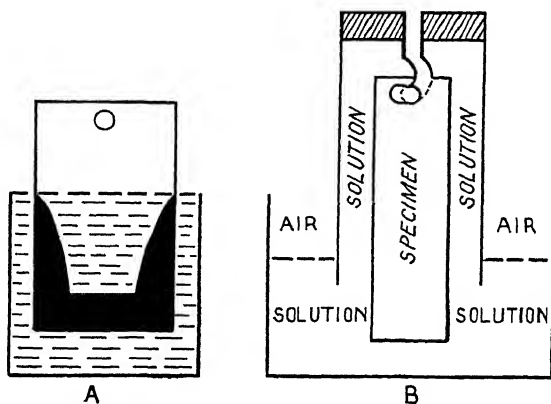
If the hydroxide thus produced is formed close to the metal surface and clings to it the result is the same as if OH' ions were discharged directly on the anodic points. In other words protective films are built up and defects in existing films repaired, and there is nothing to distinguish a secondary from a primary insoluble product. If, however, the secondary product is formed away from the metal surface, loose and comparatively porous deposits are formed. These have quite a different influence on the progress of corrosion, and examples of this are referred to in the following sections.

The Differential-Aeration Principle and its Limitations.

According to this principle, if there is a variation in the supply of oxygen at different parts of a metal surface those parts most plentifully supplied with it will become cathodic to those less well supplied, which will become anodic by difference. This principle is based in the first instance on two simple arguments. According to the first, corrosion depends on oxygen depolarization, and when there is a difference in the amount of oxygen reaching different parts of a metal surface cathodic action must proceed most vigorously where the supply of oxygen is most plentiful, and consequently anodic action must proceed elsewhere. According to the second, oxygen forms protective films in the absence of an electrolyte, and oxidizing agents in solution have the same effect (e.g. when iron is immersed in a solution of potassium chromate); it may therefore be inferred that dissolved oxygen will tend to build up such films on parts of the surface to which it has easiest access. This principle provides a ready explanation of many experimental results, and during the period 1923 to 1931 it was almost generally accepted. Its importance was first recognized by Aston (224), it was further justified by McKay (225), and in numerous investigations Evans and his associates have done much to establish its validity and extend its application. Recently, however, as a result of an extensive investigation of the corrosion of zinc, iron, and mild steel under controlled conditions, Bengough and his associates, Stuart, Lee, and Wormwell have been compelled to recognize the limitations of this principle and to develop alternative views. Some of the experiments and arguments on which this principle and objections to it have been based may now be described, partly in order to show the application of the principle, partly to give the evidence against its general application, and partly to provide examples of how corrosion proceeds under different conditions.

In 1923 Evans (226) showed that if two plates of a reactive metal such as iron, zinc, cadmium, or lead were immersed in a salt solution and connected through a milliammeter, a current was produced when air was bubbled over one of the plates. Its direction indicated that the aerated plate became cathodic towards the other, and subsequent weighing showed that it had lost less weight. This was one of the experiments on which the differential-aeration principle was originally based, but it has been further supported by numerous others.

The oxygen which reaches an immersed metal dissolves at the surface of the electrolyte and is then carried by diffusion and convection to the



215.

surface of the metal. The amount which reaches this therefore depends on the depth of immersion. If a sheet of metal is immersed vertically, the part near the surface receives a more plentiful supply of oxygen than that more deeply immersed. According to the differential-aeration principle, corrosion of such a plate should begin at the bottom and extend upwards. In numerous experiments Evans has shown that these expectations are realized. Corrosion actually begins and extends as shown in Fig. 215 A. A similar example of the effect of differential aeration is provided by the corrosion of a dry horizontal sheet of metal with drops of electrolyte resting on it. In this case the metal covered by the outer rings of the drops should become cathodic towards that part covered by the centres of the drops because of the more ready access of oxygen to the former areas. Evans has shown that if this experiment is carried out by placing drops of sodium chloride on a freshly cleaned sheet of iron, Na^+ ions are discharged on the cathodic areas and react with the water forming alkali. Samples of the liquid taken from the outside of the drops give an alkaline reaction. Cl^- ions are discharged on the anodic areas in the interior of the drops, and iron chloride is formed. Samples of the liquid abstracted by means of a capillary tube from these interiors are found to contain iron salts.

One of the most serious aspects of electrochemical corrosion is the occasional irregularity of its distribution, which leads to the formation of pits at certain points, while the rest of the metal remains substantially unattacked. This phenomenon was formerly attributed to chemical or physical heterogeneity of the metal, but this explanation though true in many cases, is in general inadequate. In the majority of instances, pitting, i.e. locally intensified corrosion, cannot be correlated either with local variations in physical properties or with the distribution of two phases. If it can be assumed that metals in their ordinary condition contain minute pores and crevices, pitting can be explained on the differential-aeration principle. There is a certain amount of direct evidence in support of this assumption, e.g. Tammann and Bredemeier (227) by means of high pressures were able to force a dye solution right into the interior of metal specimens, and in any case the existence of cavities might be expected from the way in which metals solidify. According to the differential-aeration view of pitting, oxygen dissolved in the electrolyte has easy access to the outer surface of the metal but has difficulty in reaching the inside of the minute cavities. Their sides and bottoms become anodic to the rest of the surface, and pitting is thus the widening and deepening of these by anodic dissolution. The metal salt formed therein diffuses outwards and meets the alkali formed on the surface. Insoluble metal hydroxide therefore accumulates over the mouths of the pores and further delays the access of oxygen.

In general, according to the differential-aeration principle any agent that retards the access of oxygen to certain parts of a metal surface relative to others tends to promote corrosion. Dust and other inert materials may have this effect, and particles of scale and corrosion product are also capable of acting in this way.

In the early stages of their investigations Bengough and his associates (228-33) accepted the differential-aeration principle. As the work proceeded certain results that did not agree with it were obtained, and experiments were then undertaken to ascertain its limitations. All the results thus obtained on zinc, iron, and mild steel go to show that areas where no corrosion takes place are protected by films formed in the electrolyte, but these are not formed where the supply of oxygen is greatest, nor are they the only cathodes. A large supply of oxygen to a particular area does not necessarily make it cathodic nor protect it from dissolution, and a restricted supply to another area does not necessarily make it anodic. In other words, although the continuation of corrosion requires oxygen to act as a depolarizer at the cathodes the available supply of oxygen does not determine the location of the cathodes.

In one experiment Bengough, Lee, and Wormwell (231) studied the effect of different concentrations of oxygen on two electrodes separated from each other by a porous diaphragm and connected to a potentiometer. Both electrodes were immersed in the same solution, but a considerable amount of oxygen was supplied to one (the O electrode) while

OXIDATION AND CORROSION

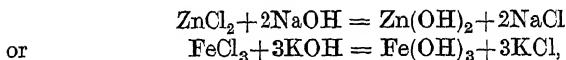
a smaller amount of air was supplied to the other (the A electrode). Various experiments were carried out in four different strengths of KCl solution, namely N/200, N/10, N/2, and 2N. In all the experiments the O electrode was cathodic at first. In some of the experiments in N/10 and N/2 solutions it remained cathodic throughout. In the other experiments a reversal of potential occurred, and in some a further reversal restored the original polarity. In N/10 solution the O electrode suffered the same loss in weight by corrosion as the A electrode. In all other experiments it lost more weight. In N/2 solution, e.g., the O electrode lost more than twice the weight of the A electrode even when the oxygen concentration was three times that at the A electrode. These experiments show that although a greater oxygen supply at one electrode makes it cathodic towards the other at the beginning of the test, this condition is not always maintained, and in any case, corrosion takes place most rapidly at the electrode most plentifully supplied with oxygen.

The above experiments were carried out under stagnant conditions, i.e. no bubbling of the gas occurred. When oxygen was bubbled round the O electrode in N/2 solution a high cathodic potential was reached, and the loss in weight of the O electrode was only one-ninth of that of the A electrode. When gas was bubbled round both electrodes the O electrode was again cathodic but it lost three times as much weight as the A electrode. In connexion with these results on the effect of the amount of oxygen supplied to the surface of the metal some experiments performed by Lee (234) may be mentioned. This investigator studied the rate of corrosion of steel under pressures of oxygen of from 1 to 25 atmospheres. In each case the amount of corrosion was a linear function of time, and the rate of corrosion as measured by the loss in weight per day was directly proportional to the pressure. No evidence was obtained that a high rate of oxygen supply produced passivity or even a decrease in the corrosion rate or a diminution of the area of attack. It was therefore concluded that oxygen in solution acts only as a depolarizer.

In the partial-immersion experiments used by Evans and his co-workers to substantiate the differential-aeration principle, corrosion of iron and steel normally begins on the three immersed edges and spreads upwards and inwards as shown in Fig. 215 A. According to the original views this behaviour is due to the gradual exhaustion of the oxygen supply from below upwards, supplemented by the effect of the corrosion product in restricting access of oxygen to the metal below it. Bengough and Wormwell (233) performed some experiments of this kind, but they were continued for longer periods than those of Evans. From the results it was concluded that the distribution of corrosion shown in Fig. 215 A is not really typical of vertically immersed conditions, and that it is easily upset by movement of the solution and other physical means. They then carried out some experiments in which the direction of the oxygen supply was reversed, so that it had most

ready access to the bottom of the specimen. The arrangement is shown in Fig. 215 B. According to the differential-aeration principle corrosion of the specimen should begin at the top and spread downwards. Actually, however, it began at the bottom and spread upwards, thus showing that the distribution of corrosion is not controlled by variations in the oxygen supply.

As the corrosion of vertically immersed specimens begins at the bottom and spreads upwards without regard to the direction of the oxygen supply, it appears that its distribution under these conditions is controlled by gravity. If it takes place at points spread over the whole surface of a specimen immersed in potassium chloride solution, soluble metallic chloride will be formed at the anodic points, and hydroxide at the cathodic points. The concentration of either of these products in the neighbourhood of the point at which it is formed will tend to retard further electrochemical corrosion. Bengough and Wormwell suggest, however, that soluble metallic chloride tends to move downwards under gravity, whilst alkali tends to spread over and cling obstinately to metal surfaces, on which protective films are formed in time if the concentration of alkali is high enough. As alkali and metallic chloride react to form an insoluble hydroxide of the heavy metal and chloride of the alkali metal, e.g.



it follows that the downward streaming chloride neutralizes the alkali below it, hydroxide is deposited on the surface of the metal, and sodium chloride is restored to the solution. On parts of the metal where alkali accumulates corrosion will be retarded, but when it is neutralized by metallic chloride corrosion can proceed. Owing to the downward movement of the chloride, alkali tends to accumulate towards the top of vertically immersed specimens and to be neutralized lower down. Thus, according to Bengough and Wormwell, the distribution of corrosion is controlled by the distribution of alkali. In support of this they describe experiments which indicate that when the alkali concentration is kept low and nearly uniform, corrosion is equally distributed over the whole surface. It seems probable therefore that differential aeration is only one of several factors which affect the distribution of alkali and the adhesion of films formed by it.

When the corrosion product does not form a thin protective film on the surface of the metal but builds up loose masses, it is considered, according to the differential-aeration principle, to promote dissolution at the points where it is formed by screening them from oxygen. This assumption requires the corrosion product to exercise selection in preventing the inward diffusion of oxygen to the metal while permitting the outward diffusion of metallic ions. It is evident that such products do not prevent the outward diffusion of metallic ions, otherwise corrosion

would cease, and Bengough and Wormwell contend that they also permit the inward diffusion of oxygen. In experiments with steel specimens immersed in potassium chloride solution under oxygen it was found that deposits of black magnetic and brown ferric oxide accumulated on the surface, and after 200 days' exposure both corroded and uncorroded areas were completely hidden. In spite of the building up of thick masses of oxides the rate of absorption of oxygen either remained constant or increased during a period of 600 days.

In experiments in which part of the metal was screened from oxygen by fine washed silver sand, results that did not agree with the requirements of the differential-aeration principle were also obtained. If a piece of steel, immersed in potassium chloride under ordinary air, is half embedded in sand, it would be expected from the above principle that the embedded part would corrode more rapidly than the top part. In one experiment corrosion occurred on both parts for a day or two, after which it almost ceased on the embedded part but was quite active on the exposed part. In a similar experiment carried out under oxygen more corrosion occurred on the embedded part, and the same result was obtained when air freed from acid gases was used. Evidently, the balance is somewhat delicate and swings in one direction in ordinary air, and in the other in purified air or oxygen. Further experiments showed that a mixture of purified air and carbon dioxide behaved like ordinary air, while one of purified air and sulphur dioxide gave results that seemed to be determined mainly by factors connected with the metal surface. Thus a thin emery-ground specimen with cut edges showed most corrosion on the exposed part, but a rectangular specimen milled on all faces was corroded only on the embedded parts. The explanation of these results seems to be that the distribution of corrosion is determined by the greatest difference of potential that can be set up between any two parts of the specimen. Sometimes this will be between two parts of the exposed surface, and at others between the embedded part as a whole and the exposed surface. The presence of carbon dioxide tends to destroy protection on the part exposed to oxygen, which therefore becomes the most corroded.

One of the most important features of the differential-aeration principle is the explanation of pitting that is provided by assuming that pores and crevices are originally present in the metal and that corrosion takes place preferentially at these places because oxygen has less access to them. According to Bengough and Wormwell this view is at variance with many known facts about the initiation and subsequent changes of corrosion distribution and intensity in alkali chloride solutions. Corrosion of cast zinc and rolled mild steel normally begins at very numerous sporadically distributed centres, but it soon ceases at those situated in certain well-defined areas and continues at those in other areas. It is most improbable that crevices are confined to the latter, since the distribution of the areas is largely a matter of the arrangement of the

specimen in the liquid. Consequently, crevices cannot normally be an important factor in the distribution of corrosion. A further objection is that pitting only occurs exceptionally, whereas, according to the above view it should be an ordinary feature of corrosion and metals should be quickly perforated.

The same authors describe several observations that indicate the limitations of the original view of the effect of pores and crevices. They found that when a zinc specimen was first corroded till definite and easily visible pits were formed, then removed, stripped of corrosion product and thoroughly cleaned, corrosion on subsequent immersion did not begin at the original pits, but at new centres which gave rise to an entirely new set of pits. On specimens of zinc and mild steel finished with a fine cut on a precision lathe the attack in the first place was nearly sporadic, but the most active centres in dilute solutions of sodium and potassium chlorides or sulphates were often tears and burrs situated at the crests of the tool-marks and not in the troughs. In general, chemical composition appeared to have a more important influence on the localization of attack than visible or invisible crevices. On very highly purified zinc etch pits were formed on crystal faces, but on less pure metal the deepest attack was usually along crystal boundaries. Corrosion sometimes occurred at cracks in metals, but in all the specimens examined it was located not at the bottom of the cracks, as would be expected from the differential-aeration principle, but at the edges at the top.

The general conclusions of Bengough and his co-workers on differential aeration may be summarized as follows: When corrosion is irregularly distributed the areas where no corrosion takes place are protected by films formed on the metal, and those where corrosion does take place are not protected by films. The distribution of protective films controls that of corrosion, but the distribution of dissolved oxygen does not alone control that of protective films, i.e. these films are not confined to well-aerated areas nor are they absent from less aerated areas. The spread of alkali, the presence of reactive areas in the metal, the action of gravity and other factors affect film distribution which often undergoes important changes with time, although the nature of the oxygen supply has not been altered. When the protective films are widespread, corrosion may be sufficiently localized to be called pitting. When the films are restricted, corrosion is spread out over areas which vary with the experimental conditions and with time, and may finally cover the whole surface of the metal.

Film Formation and Alkali Distribution.

It is evident from the experiments just described that the differential-aeration principle cannot be held to be generally applicable, and some other explanation of the distribution of corrosion is required. The view of Bengough and his associates is that the distribution of protective

films depends on that of the alkali formed at cathodic points, and that the distribution of this depends in turn on several factors one of which is differential aeration. In the case of a vertically immersed plate, e.g. the only part to which oxygen has easy access is near the water line, and it is there that the main cathodic reaction occurs. This is where the main supply of alkali is formed and thus differential aeration is one of the factors that indirectly controls the distribution of corrosion in this case. But differential aeration is not the only factor affecting the distribution of alkali or protective films and therefore great care must be exercised in attributing results to it. The following general account of the factors affecting the distribution of corrosion may therefore be given.

When a specimen, on which no air-formed or other appreciably protective films are present, is immersed in an electrolyte, the distribution of the centres of corrosion is at first quite at haphazard. Bengough, Lee, and Wormwell (231) studied the corrosion of zinc under a microscope. They observed that in the early stages, corrosion took place at a very large number of sporadically distributed centres. A change soon set in, however, and many of the original centres ceased to function. From those which remained active corrosion was observed to spread outwards. All subsequent corrosion took place at and around them, and no new centres were formed. When Australian electrolytic zinc was used, the active centres at which corrosion settled down after the original sporadic distribution were mainly located at the crystal boundaries. This metal contained about 0.01 per cent. of impurities, mainly lead and iron. When highly purified zinc, which was shown by spectroscopic examination to be free from metallic impurities, was used, there was no attack at the crystal boundaries. The active centres were situated on the surfaces of the crystals.

Examination of zinc specimens after corrosion showed that in dilute solutions of potassium chloride and potassium sulphate the attack was confined to certain areas, and around these interference-colour films were formed. Even when the attack was continued for a long period certain parts suffered relatively little corrosion. In stronger solutions the attack extended from the original centres, and with increase in strength of the solution the area of unattacked surface decreased. In some experiments these areas ultimately disappeared entirely, and as this was not accompanied by any diminution in the rate of corrosion, as measured by the amount of oxygen required for cathodic depolarizations, it is evident that these were not the only cathodes. As the extension of the attacked areas resulted in the accumulation of corrosion products over the whole or the greater part of the surface without diminution in the rate of attack, it is evident that the product did not prevent access of oxygen to the underlying metal.

The corrosion of iron and mild steel was found to follow a similar course. On a steel specimen immersed in N/100,000 KCl, corrosion

started at a large number of sporadically distributed centres, about 1,500 per sq. cm., as estimated at the end of 2.5 minutes. At the end of 2.5 hours most of these had ceased to function, and thereafter corrosion was confined to a relatively small number of points. In N/10,000 KCl the corrosion of steel began at about 10,000 centres per sq. cm. On purified iron the number was reduced to 1,200 per sq. cm., and heating the steel to 185° C. for 30 minutes before immersion reduced the original number of active centres to 2,000. As the attack on the unprotected steel progressed, many of the original centres ceased to function, and the final distribution of corrosion was quite different from the original. In N/10 KCl, corrosion started at fewer centres than in weaker solutions, but it spread rapidly from them, and after long periods of exposure the whole surface was attacked.

In the absence of previously formed protective films, corrosion begins at a very large number of centres, the distribution of which is to some extent determined by chance. Anodic and cathodic areas are not distinguished from each other by any recognizable physical or chemical feature. At the anodic areas metallic salts are formed. At the cathodic areas alkali is formed. By the reaction between these products metallic hydroxide is formed. The OH' ions from the alkali, and the metallic hydroxide formed as a secondary product are capable of forming protective films if they are discharged or precipitated on the metal surface. It is in this way that certain areas become protected, and the mechanism of this protection is such that it may be produced with equal facility on areas that were originally either anodic or cathodic. If the metal is easily protected, i.e. if it readily forms an insoluble hydroxide, a protective layer is built up over the whole surface. This is what occurs in the case of stainless steel, aluminium, nickel, and chromium. On metals that are not easily protected a certain number of active areas remain. Thus, Forrest, Roetheli, and Brown in studying the corrosion of ordinary and stainless steel found that both materials were at first attacked at the same rate when initially in a film-free condition. But on the stainless steel the velocity of attack soon died away, owing to the building up of a protective film, whilst the high rate of attack on the ordinary steel continued.

It is probable that in many cases when easily protected metals exhibit no visible evidence of corrosion, some reaction is still taking place at discontinuities spontaneously formed in the films. Whenever any dissolution takes place at a pore or a crack, however, the discontinuity is immediately closed by the discharge of OH' ions or the precipitation of hydroxide. In other words the films formed do not provide permanent protection unless the conditions are such that they are kept in repair. This requires the presence of alkali, and the more pervious a film is and the weaker its adhesion to the surface of the metal, the greater is the amount of alkali required. The films formed on iron and zinc need constant repair. Consequently, they do not provide efficient protection

unless corrosion leading to the production of alkali is going on somewhere. Thus although the areas on which protective films are formed may be chemically and physically indistinguishable from those at which the attack proceeds, all areas cannot become protected except in solutions which contain high concentrations of OH' or other anions that form insoluble anodic products.

When iron, steel, or zinc are immersed in salt solutions or natural waters some areas become protected in the initial stages of corrosion whilst others do not. Corrosion is thus confined to certain areas. If the concentration of Cl' or SO_4'' ions is small, corrosion will continue to be confined to those areas whilst the protective films are kept in repair. If, however, their concentration is great, corrosion will spread by undercutting and penetration of the protective films until no areas are effectively protected. If the specimens are withdrawn from the electrolyte the mechanism of repair ceases to operate, and the films already formed over certain areas will tend to become porous or to be destroyed by any treatment used to clean the specimen. On reimmersion corrosion will therefore start at new centres. If, on first immersion, the conditions were uniform over the whole surface of the metal and throughout the electrolyte in contact with it, and if there were no convection currents in it, then the distribution of protected and unprotected areas would be determined by chance. But these conditions can seldom be realized, and there will usually be some areas on the metal surface more active than others or on which protective films cannot be formed. Thus the presence of even 0.01 per cent. of impurity in zinc makes the crystal boundaries more active than the body of the crystals, and burrs, ragged edges, cut edges, tool-marks, &c., tend to localize corrosion because films are not readily formed on them. In the case of tool-marks it is not in the troughs but on the crests that attack tends to be localized, and in the case of cracks it is not at the bottom but on the edge at the top that preferential corrosion occurs. Convection currents affect the distribution of corrosion by moving the corrosion product and thus influencing the location of precipitated hydroxide. According to the 'film-control' view of the distribution of corrosion the action of substances in contact with the surface is to prevent the formation of surface films. Thus particles of dust or non-adherent corrosion product may promote corrosion where they are deposited, not by preventing access of oxygen but by inhibiting the formation of film.

THE RATE OF CORROSION

A list of the factors that affect corrosion has already been given, and it may be pointed out that these influence the rate as well as the distribution. The factors tabulated refer, however, to specimens wholly immersed in stagnant solutions, and under other conditions other factors intervene. When, e.g., metals are exposed to moist but unsaturated air containing the usual impurities, the presence of moisture accelerates

corrosion, but not to an appreciable extent unless the critical humidity of the corrosion product is exceeded. Under these conditions this factor is important and it remains so even when the metal is exposed to dew-point conditions. When a metal is subjected to direct rainfall the washing-away of the corrosion product becomes a factor to be considered, and the critical humidity loses some of its importance. Under conditions of partial immersion the tendency of protective films to peel off at the water-line sometimes leads to serious corrosion at this point, particularly when the immersed metal is to some extent protected. Finally, the influence of many factors is completely altered when strong convection currents occur, or when the electrolyte is agitated or caused to flow continuously over the metal.

Many methods have been adopted in investigating the rate of corrosion of different metals under different conditions. In so far as the conditions of exposure are concerned, three different kinds of experiments may be distinguished—field tests, accelerated tests, and experiments under controlled conditions. In field tests the metals under investigation are exposed to conditions that imitate as nearly as possible those that they will be expected to resist in service. The results of such tests are very difficult to interpret. It is generally considered that they give a relative idea of the service that may be expected of the metal when used under conditions similar to those realized in the test. But as these are not accurately known it is impossible to say what 'similar conditions' are. In general, no very convincing conclusions have directly emerged from field tests, and the same is broadly true of accelerated tests in which an endeavour is made to assess the relative corrodibilities of metals by exposure to conditions that produce rapid dissolution, e.g. solution in acids. Very few experiments under controlled conditions have been carried out, for the necessity for them has not long been appreciated, and they are so different from those of service that many years' patient work must be anticipated before results of direct practical application can be expected. During the last ten or twelve years, however, experiments of this kind have been carried out by Bengough and his associates, first at the Royal School of Mines and later at the Chemical Research Laboratory, Teddington. In the meantime, knowledge of the relative corrodibilities of different metals is based on the accumulated information that has been obtained by observation of their behaviour in service, in innumerable field tests, and in qualitative laboratory tests. In general, the noble metals (platinum, gold, and silver) and those that possess the property of forming adherent protective films (nickel, chromium, aluminium, tin, lead, and cobalt) are the most resistant to corrosion, and tend to confer a high resistance on alloys in which they are present in solid solution. A reactive metal such as iron which does not form a protective film, does not resist corrosion, and the same applies to a less extent to many two-phase alloys containing more resistant metals. The practical importance of corrosion is due to the fact

that the most widely used alloys, i.e. steel, cast iron, brass, and strong aluminium alloys, are liable to suffer deterioration under many conditions when it is otherwise convenient to use them, and even the ordinarily resistant alloys, e.g. stainless steel and nickel-copper alloys, are liable to be adversely affected under certain conditions.

With regard to the methods adopted for measuring corrosion it may be said that the usual procedure is to expose weighed specimens for a definite time to the corroding medium and then to determine the change in weight. If the corrosion product adheres firmly to the specimen, the increase in weight may be measured, as in cases of tarnishing in atmospheres of low humidity. But when the metal is exposed to rain some of the corrosion product is washed away, and in total-immersion tests some of it goes into solution. In these cases it is necessary to determine the decrease in weight after the still-adhering corrosion product has been removed. An alternative method is to use wire and strip specimens and to measure the increase in electrical resistance due to the reduction of the effective metal cross-section by dissolution. The most satisfactory method, however, is to follow the progress of corrosion by making determinations from time to time without interrupting the experiments or altering the conditions to which the metal is exposed. This can be done by measuring the amount of hydrogen evolved and of oxygen absorbed in the cathodic reactions. Bengough and his associates have employed this method throughout their experiments.

Although the rate of corrosion is affected by numerous factors they are not all of equal importance, and in most cases one factor may be distinguished as exerting a dominant influence whilst the others simply modify its effect. Evans calls this the controlling factor, and it may be described as that factor which compels the slowest rate of attack. When, e.g., active metals are immersed in oxygen-free solutions the progress of corrosion depends on the evolution of hydrogen from cathodic areas. This in turn depends on the hydron concentration of the solution, the electrode potential, overpotential, and surface condition of the metal and the presence or absence of second constituents with noble potentials and low overpotentials. If a metal with its surface prepared in a given way is immersed in a solution of low hydron concentration the rate of corrosion will be slow and will be controlled by that factor. If this is suitably increased the overpotential of the metal will become the controlling factor if no noble constituents of low overpotential are present. But if these are present, the electrode potential of the metal will become the controlling factor. The reactive metals iron and zinc liberate hydrogen very slowly from pure water, and the rate of liberation increases with increase in the hydron concentration of the electrolyte. In general, however, electrochemical corrosion requires the presence of oxygen to promote cathodic action by combining with hydrogen. Under totally immersed conditions the supply of oxygen to the surface of the

metal is a slow process, and the rate of oxygen supply is the controlling factor, but in atmospheric corrosion a plentiful supply of oxygen is available, and the controlling factor is then the electrical conductivity of the film of moisture condensed on the surface of the metal.

The above factors can only exert their controlling influence when the metals concerned are not capable of forming highly protective films over their whole surface under the conditions realized. If these are formed they become the controlling factor. If they are completely impervious to ions and maintained in repair, corrosion ceases wherever they occur. If they are porous and subject to periodic failure corrosion proceeds slowly. Protective films formed over certain parts of the surface have a pronounced effect on the distribution of corrosion, and they may also retard the rate of total corrosion when this depends on hydrogen evolution or the conductivity of a layer of condensed moisture, but when the rate of corrosion is controlled by that of the supply of oxygen the protection of certain areas does not retard the rate of total corrosion. It simply causes the attack to be concentrated on unprotected areas. The effect of corrosion products other than adherent impermeable films depends on their nature and position. Sometimes they exert no effect, but frequently they retard corrosion by delaying the movement of anions and metallic salts to and from the surface of the metal.

The rate of corrosion is controlled by the supply of oxygen so long as that which reaches the surface of the metal is used up as rapidly as it is supplied, so that the layer of liquid in contact with the metal is kept practically free from it. If the rate of its supply can be increased to such an extent that it begins to accumulate at the surface of the metal then it is no longer the controlling factor, and the dominant influence is exerted by the conditions at the anodes. If several metals are deeply immersed in a solution, and the conditions are such that no hydrogen is evolved and all the oxygen supplied is used up as quickly as it arrives, the rate of dissolution of the different metals will be proportional to the amount of metal required to displace a given amount of hydrogen, i.e. the rate of dissolution measured in gram-equivalents will be the same for all the metals. If the rate of oxygen supply is decreased that of corrosion will also decrease. If, however, it is increased, some oxygen will eventually begin to accumulate at the surface of the least active metals and their rate of corrosion will no longer increase with its supply. The corrosion of the more reactive metals will continue, however, to be accelerated by increase in the rate of supply of oxygen until this becomes so plentiful that it cannot be used as fast as it arrives. Under these conditions no further acceleration takes place. In practice, however, surface films soon interfere with the corrosion of many metals, and the process comes to a stop irrespective of the amount of oxygen supplied. Oxygen control therefore applies only to active metals like iron and zinc under conditions that do not permit the formation of protective films.

In these cases the rate of supply to immersed surfaces cannot readily be increased to such an extent that it begins to accumulate at the surfaces. Here, therefore, except in so far as it is supplemented by hydrogen evolution or retarded by accumulated-corrosion product, corrosion does depend on oxygen supply.

Oxygen dissolved at the surface of a stagnant solution is conveyed to an immersed metal by convection currents and diffusion. As its solubility in water and salt solutions is low, the amount reaching the surface of immersed metals is small. It depends, however, on the pressure of oxygen over the surface of the solution, the depth of immersion of the metal, and to a certain extent on the area of the liquid-gas interface. Increasing the pressure of oxygen over the solution raises the rate of supply to the metal. This condition does not arise in service, but tests under increased pressure throw some light on what may be expected in moving solutions when a fairly rapid supply of oxygen is maintained.

When metals are exposed to the action of the atmosphere a plentiful supply of oxygen is available for cathodic action, and oxygen supply is not the controlling factor. Under these conditions the rate of corrosion is determined by the conductivity of the layer of moisture on the surface of the metal and the nature and distribution of the corrosion product. Pure water and air alone are capable of producing a sensible amount of corrosion on iron and steel, but in the absence of polluting agents the action is exceedingly slow even when the precipitation of moisture is considerable. This is because the conductivity of pure water is very low, and the only anions present are OH' ions which form a slightly soluble corrosion product. In regions where the atmosphere is pure, e.g. in the Alps, exposed steel-work suffers very little attack. In urban and industrial regions, however, the atmosphere is polluted from the combustion of coal, and in the vicinity of the sea it contains chlorides. These substances dissolve in the moisture condensed or precipitated on metals, and serve to increase the conductivity of the liquid film and also to form more soluble anodic products. Thus to a certain extent the atmospheric corrosion of metals is determined by the impurities in the atmosphere to which they are exposed, but the other factors mentioned in the sections dealing with direct oxidation must also be considered.

Corrosion-Time Curves.

When a freshly cleaned specimen of corrodible metal is immersed in a solution in which protective films are formed, corrosion begins fairly rapidly, but the rate soon diminishes and becomes very slow before an appreciable amount of metal is affected. Corrosion-time curves for such conditions are similar to those obtained when copper is exposed to direct oxidation (e.g. Fig. 201). Periodic break-down of the protective film results in periodic acceleration of the rate of attack, but this is soon decreased again by the automatic repair of the film. This phenomenon

gives rise to steps in the corrosion-time curve similar to those shown in Fig. 206 representing the atmospheric corrosion of aluminium. When protective films are not formed over the whole surface, corrosion proceeds continuously, and the progress of the attack is a linear function of time. The slope of the corrosion-time curve then depends on the rate of evolution of hydrogen, the rate of supply of oxygen, or the sum of these two factors. In laboratory experiments with small quantities of

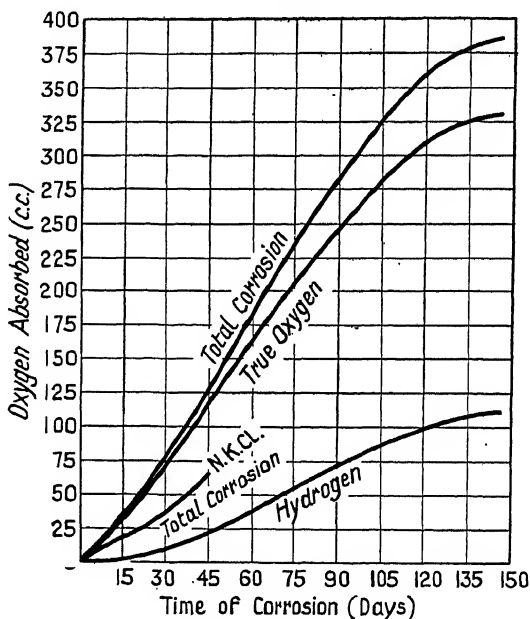


FIG. 216. Corrosion-time curves for zinc in N/10 KCl.
(*Journal of the Society of Chemical Industry.*)

stagnant electrolyte the rate of corrosion may decrease after a time as a result of the diminishing concentration of the ions required for anodic action, or because of the accumulation in the electrolyte of salts of the corroding metal, but if neither of these factors interferes with the attack, and the supply of oxygen is maintained, corrosion will continue at the same rate until the corrosion product adhering to the surface of the metal begins to retard the movement of ions and the diffusion of oxygen or hydrogen.

Curves of the corrosion of zinc in N/10 potassium chloride are shown in Fig. 216. These were obtained by Bengough by measuring the amounts of oxygen absorbed and of hydrogen liberated. Except for a slight change in slope at about 70 days, the curve for oxygen absorption is linear over the period from 20 to 105 days. The curve for hydrogen evolution is approximately linear from 30 to 120 days. As the liberation of two volumes of hydrogen is equivalent to the absorption of

one volume of oxygen, the curve for total corrosion in terms of oxygen absorbed is obtained by adding half the volume of hydrogen to that of oxygen. The curve for hydrogen evolution shows a marked period of induction during the first 30 days. As explained earlier this is due to the gradual accumulation of noble impurities which promote the liberation of this gas. The diminution of the rate of attack after 105 days is due to the partially protective effect of adhering-corrosion product.

In some other experiments Bengough and his co-workers showed that

CURVES.

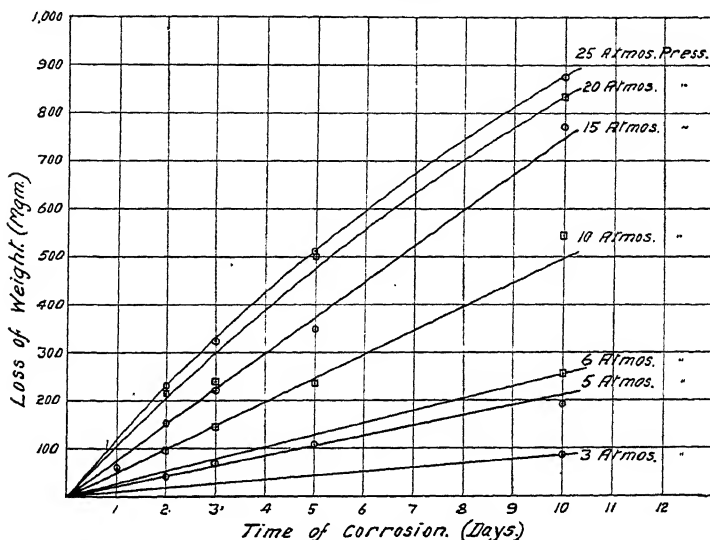


FIG. 217. Corrosion-time curves for steel under different oxygen pressures.

(*Journal of the Faraday Society.*)

the slope of the curve for oxygen absorption became steeper as the supply of oxygen was increased. This was done by decreasing the depth of immersion or increasing the area of the oxygen-liquid interface. The influence of oxygen supply is most clearly illustrated, however, by some experiments performed by Lee (234) who determined the loss in weight with time of mild-steel specimens immersed in N/10 potassium chloride solutions under different oxygen pressures. The corrosion-time curves are shown in Fig. 217. Up to 20 atmospheres the curves are linear, but at 25 atmospheres the corrosion rate decreases with time. Lee observed that this change in the shape of the curve coincided with one in the nature of the corrosion product which, under a pressure of 25 atmospheres was hard and granular as compared with the loose product formed at lower pressures. From the straight-line curves of Fig. 217 the mean rates of corrosion were calculated, and the relation between the rate of corrosion and oxygen pressure is shown in Fig. 218.

As a final example of corrosion-time curves those obtained by

Bengough and Lee (235) for the corrosion of steel in sea-water may be described. Contrary to what had been previously supposed, these investigators found that the corrosion of steel in sea-water was accompanied by the liberation of substantial quantities of hydrogen. In the absence of oxygen no liberation of hydrogen occurred, so that steel immersed in oxygen-free sea-water was not attacked. In the presence of oxygen, however, hydrogen was evolved, and the absolute rate of

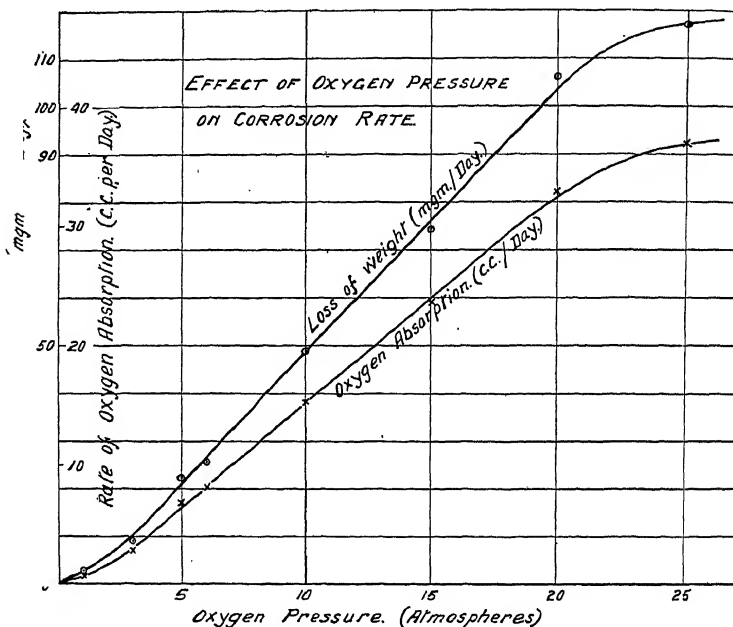


FIG. 218. Effect of oxygen pressure on corrosion rate.
(*Journal of the Faraday Society.*)

evolution was practically independent of the oxygen supply. As the rate of corrosion due to oxygen increased with the supply, while that due to hydrogen evolution remained constant, the proportion of the total corrosion due to hydrogen evolution decreased with an increase in oxygen supply. Thus in one experiment the corrosion due to hydrogen evolution was about 60 per cent. of the total, whereas in another with an increased supply of oxygen it was only 10 per cent. Sea-water corresponds approximately to an N/2 sodium-chloride solution, but in such a solution, and in others to which magnesium and calcium chlorides were added to obtain a closer approximation to sea-water, a much smaller evolution of hydrogen was obtained. It was therefore concluded that the marked evolution of hydrogen in sea-water was associated with the presence of organic matter. A set of corrosion-time curves for mild steel (0.13 per cent. carbon) in sea-water and sodium chloride under oxygen is reproduced in Fig. 219.

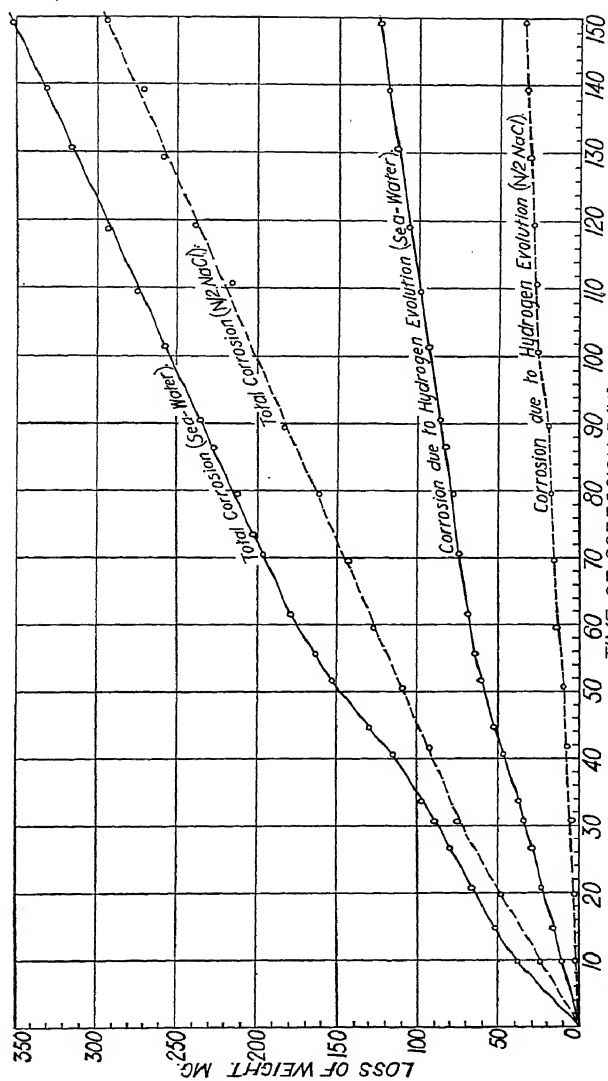


Fig. 219. Corrosion-time curves for steel in sea-water and N/2 NaCl.

(Journal of the Iron and Steel Institute.)

PROTECTION AGAINST OXIDATION AND CORROSION

The most effective protection against direct oxidation or electrochemical corrosion is obtained by the use of metals that exhibit a high degree of resistance either to chemical attack in general or to the particular conditions to which they will be exposed. Such metals may be classified in three groups.

1. Noble metals, such as gold, platinum, and silver, which have a low affinity for oxygen and a positive electrode potential. Owing to their high cost these metals are not available for general use. Gold is used in jewellery and dentistry, platinum for jewellery and laboratory ware, and silver for table-ware and also to some extent in the lining of vessels used in the manufacture of food-stuffs. Copper is the only noble metal available for extensive application, and it is used for many purposes for which steel is unsuitable, but its general resistance to corrosion is distinctly less than that of some of the metals in the next group.

2. Passive metals, such as chromium, nickel, cobalt, aluminium, silicon, lead, and tin, which have a fairly high affinity for oxygen and a negative electrode potential, but exhibit a high degree of resistance to corrosion because of their ability to form protective films. For many purposes materials of this kind are eminently suitable, but it should always be borne in mind that the resistance to corrosion is not due to the intrinsic inertness of the metal, but to a particular relationship between the metal and its environment. If the conditions of exposure do not permit the formation of, or cause the break-down of, the protective films, a high resistance to attack cannot be expected.

3. Alloys in which the resistance to corrosion of the basis metal is increased by the presence in solid solution of a more highly resistant metal.

Copper is not sufficiently noble to constitute a corrosion-resisting material, and the application of the other metals of the first group is restricted by their price, so that the industrially useful corrosion-resisting metals are consequently those included in the second and third groups. The pure metals nickel and aluminium are fairly widely used where resistance to corrosion is required, chromium, nickel, cobalt, and tin are used as coatings on other less resistant metals, but the most widely employed corrosion-resisting metals are the alloys in the last group. Of these the most important are the stainless steels which are essentially steels containing chromium, but nickel is frequently a constituent, and molybdenum, tungsten, silicon, aluminium, and copper are occasionally added. To obtain a high resistance to corrosion the chromium content should exceed 11 per cent., and the steel should be heat treated so that it consists of a solid solution of the chromium in iron. But an increased resistance to corrosion over that of ordinary steel is obtained with as little as 4 per cent. of chromium even when the

steel does not consist of a solid solution and in the absence of other corrosion-resisting metals. The nickel-chromium stainless steels pass almost imperceptibly into the nickel-chromium-iron alloys by the elimination of carbon, and these in turn pass into the nickel-chromium alloys. Both groups have a high resistance to corrosion.

Corrosion-resisting cast irons are made by adding chromium and nickel in about the same proportions as in stainless steel, but a particular type of cast iron which exhibits a high resistance to acids is made by adding 14.5 per cent. of silicon. Other important corrosion-resisting alloys are the nickel-copper alloys, the nickel-copper-zinc alloys, the copper-aluminium alloys, the copper-tin alloys, aluminium-brass, cobalt-chromium-tungsten alloys such as stellite, and iron-aluminium alloys.

When conditions of cost, weight, or mechanical properties make it impossible to use such alloys, less resistant metals are preserved against attack by coating with a protective layer of another metal, with paint, bituminous material, enamel, grease, or with a film of oxide, phosphate, or other compound. Metallic coatings may be formed by rolling composite sheets, as in coating steel with nickel (Niclاد), or aluminium alloys with pure aluminium (Alclad). They may also be formed by dipping the metal to be protected into a molten bath of the protecting metal as in the manufacture of tin-plate and galvanized articles. Protective metallic coatings may also be formed by electro-deposition of the protecting metal as in silver-plating, nickel-plating, and chromium-plating. Finally, articles may be coated with zinc, aluminium, or chromium by heating in metallic dust, the processes being known respectively as sherardizing, calorizing, and chromizing, or they may be coated with practically any metal by spraying.

There are certain disadvantages inherent in the use of metallic coatings. In the first place some of the metals used are themselves by no means incorrodible in polluted atmospheres. Nickel and zinc, e.g., are both attacked by moist air containing sulphur dioxide. Furthermore, such coatings, however applied, are liable to be distinctly porous because of the presence of pin-holes, and in any case there is always the danger that the coating will be broken at certain points by abrasion during service. When discontinuities in the protective coating lead to the exposure of the underlying metal, electrical couples are likely to be set up at the points of contact of the dissimilar metals. If the protecting metal is more noble than the underlying metal, e.g. if steel is coated with tin, nickel, or copper, penetration of the coating leads to preferential corrosion of the former. If, however, the coating is less noble it will corrode preferentially, and the underlying metal may receive a certain amount of cathodic protection. This is one of the advantages of zinc coatings on steel, for even when the protective layer is penetrated, serious corrosion of the steel does not take place until substantial amounts of the zinc have been removed.

The protection of metals with paints, enamels, bituminous materials,

and greases cannot be dealt with in this book, but some of the methods of protecting them with oxide and other films may be mentioned. One of the most important of these is the anodic protection of aluminium and its alloys. In this process, which was devised by Bengough and Stuart, the articles to be protected are made the anodes in a bath of three per cent. chromic acid. Carbon cathodes are used, and an impervious adherent oxide-film is formed on the aluminium by the anodic action of the chromic acid. This coating greatly increases the resistance of aluminium alloys to corrosion and it also acts as an excellent base for protective enamels. As the oxide can serve as a mordant for dyes of the 'alizarine' class, colour effects can be obtained by immersing anodically treated articles in suitable dyes.

Several methods are used for producing protective oxide, nitride, or phosphate coatings on iron and steel. If these metals are heated to a suitable temperature in air, with nitre, or under other oxidizing conditions, a fairly thick oxide coating may be produced. The thickness usually aimed at is that which gives blue interference colours, and the process is known as 'blueing'. Coatings thus produced provide a certain amount of resistance against corrosion in the atmosphere, but in many cases the treatment is employed for decorative purposes. Numerous methods are used to produce comparatively thick coatings of magnetic oxide (Fe_3O_4) on iron and steel. In the Bower-Barff process the articles are heated to 900°C ., then exposed to superheated steam to form the oxide, and afterwards in coal gas which serves to reduce any ferric oxide (Fe_2O_3) to magnetite. Similar coatings may be produced by immersion in a bath of fused potassium or sodium nitrate containing manganese dioxide, or by anodic treatment in a solution of sodium ferrite. The nitriding process in which a layer containing nitrides is produced by heating in ammonia is mainly used to produce a hard surface, but it also increases resistance to corrosion. Finally, in the 'coslettizing' process a protective film of iron phosphate is formed by boiling the articles under treatment for some hours in a solution of phosphoric acid saturated with ferrous phosphate.

An interesting method of protecting magnesium alloys against corrosion has recently been developed at the Chemical Research Laboratory. Magnesium is the lightest and the most active of the metals available for structural purposes. Because of its lightness the use of alloys in which it is the main constituent is of considerable advantage in certain parts of aircraft, but its susceptibility to corrosion has seriously retarded its application. By immersion in a bath of sodium selenite and selenious acid a protective coating of selenium is formed on this metal and its alloys. Further protection is obtained by applying a coating of enamel. Other methods of protecting metals against corrosion are mentioned in Part VI, and the subject is fully dealt with in *Protective Films on Metals* by Hedges (605). In concluding this chapter mention must be made of the book on *Metallic Corrosion, Passivity and*

Protection by Evans (606), which appeared while this book was in the press. It gives a full and well documented account of the phenomena discussed in this chapter. Finally, in another recent work on the *Corrosion Resistance of Metals and Alloys*, McKay and Worthington (607) give an account of the behaviour in different media and under different conditions of exposure of most of the commonly used metals and alloys.

PART IV

THE TREATMENT OF METALS

CHAPTER IX

CASTING

INTRODUCTION TO THE TREATMENT OF METALS

THE mechanical, chemical, electrical, thermal, and other properties that determine the behaviour of a metal in use are directly related to its nature (i.e. its composition, constitution, microstructure, crystal structure, and condition), and the last four of these attributes are in turn related to the composition of the metal and the treatment it has received. It is with properties, nature, treatment, and composition and the relations between them that this book is concerned, and having dealt generally with the first two in Parts I to III, it remains to deal generally with treatment in this part before going on to consider in Parts V and VI the complete scheme of relationships in terms of specific metals and alloys.

The treatment of metals may be said to cover all the operations performed after a melt of the requisite composition is prepared. Of these the most important and widely applied are casting, hot- and cold-working, heat treatment, and machining, but welding, soldering, brazing, and surface treatments such as tinning, galvanizing, carburizing, nitriding, anodizing, electro-deposition, &c., also come within its scope. The general object of treatment is to shape the metals, and at the same time confer on them the properties required in service in so far as these are not determined by the composition of the metal as it leaves the melting furnace. Casting, hot-working, and cold-working affect both shape and properties, heat treatment affects properties only, and machining affects shape only. Surface treatments are used to increase the hardness or corrosion resistance of metals, and they influence the properties but not the shape, while welding, soldering, and brazing are methods of building up more intricate structures from simple components and may therefore be said to be methods of shaping. Owing to the fact that the metal in the vicinity of a weld is heated during the operation, its properties are frequently modified, but this is an incidental effect of welding.

The production of the required shape by casting, working, machining or welding is always essential, but the importance of properties varies. In the manufacture of pressure die-castings from zinc-base alloys, the main purpose is to produce quickly and cheaply articles of a specified shape with the satisfactory surface associated with this method of

production, and in this case it is not necessary to obtain high strength. On the other hand, in the manufacture of aero-engine components such as valves, connecting-rods, or crankshafts, the production of the required shape is regarded as relatively simple as compared with the care and attention necessary to obtain the desired properties. These are, of course, extreme cases, but they serve to show how the importance attached to treatment as a means of influencing properties may vary. There are some shapes that can only be produced by casting, and castings have to be used unless it is found advisable to build the shape by welding together simple parts produced by working. There are other shapes such as long rods, thin sheets, and wire that can only be made by mechanical working, and this method must be used. But the majority of the shapes produced can be made either by working or casting, and when the former method is used it is because better properties are thus obtained.

For present-day purposes numerous metals and alloys are made and formed into a vast number of shapes, and in making each of the required metallic parts the treatment employed is modified in one way or another so that the finished article will display the properties appropriate to its use. In making a given article from a given alloy several different sequences of operations may be employed in different plants. In making different articles from the same alloys numerous variations of operations may be performed, and the same holds true for making the same article from different alloys. When the operations employed in making all the different metallic parts from all the different alloys available are considered, the possible combinations of casting, working, heat treatment, machining, welding, and other operations are well-nigh innumerable, and it would be impossible to deal with even a small fraction of them in this book. But although there is a great variation in the actual sequence of operations performed on different metals intended for different purposes, and in the details of the operations performed, the general features of each operation remain substantially the same. Thus the process of casting involves the same factors whether the metal is used as cast or subsequently worked, and hot-working involves the same factors whether the metal is subsequently cold-worked or not. It is therefore possible to describe the essential features of the operations performed on metals in preparing them for use without going into details about the manufacture of specific articles from particular metals or alloys.

Three aspects of metal treatment may be distinguished, namely, plant, technique, and the phenomena involved. Plant embraces the furnaces in which the metals are melted, the moulds in which they are cast, the furnaces in which they are heated for hot-working, or before, during or after cold-working, the rolling-mills, presses, stamps, &c., in which they are mechanically shaped and the furnaces in which final heat treatments are performed. It also embraces numerous accessories

used in handling masses of metal of varying size; instruments for indicating and recording temperatures; pickling equipment, foundry appliances, die-casting machines, forging and casting dies, quenching baths, &c. Technique includes such branches of the metallurgical art as the design and manufacture of patterns, moulding, control of melting and casting conditions, selection and control of heating temperatures, the design of rolls, presses, and dies, the preparation of heat treating, hot-working, and cold-working cycles, and so on. It is obviously impossible to consider all this in the present book, and as we are mainly concerned with treatment as affecting condition, structure, constitution, and properties, consideration will be confined to the phenomena involved, i.e. to the behaviour of metals in casting, working, and heat treatment; and plant and technique will only be dealt with as far as is necessary to illustrate the description of behaviour.

In the opening chapters we dealt with the crystal structure and microstructure of pure metals and the effect on them of mechanical forces applied under different conditions. Following this we considered the constitution and structure of alloys and the effect of variations in these on response to mechanical forces. Finally, we considered the mechanical and chemical properties of metals. Throughout all these chapters the presentation has been simplified by confining attention strictly to the subject-matter under consideration and neglecting certain other factors that intervene in practice. Thus, e.g., the solidification of alloys was dealt with without regard to the fact that a temperature gradient exists in all masses of cooling metal, that inclusions which are always present in the melt frequently exercise a pronounced effect on solidification, and that the process of freezing is generally accompanied by the evolution of gas. Similarly, the behaviour of metals when subjected to force was described on the assumption that metals could be regarded as compact aggregates of crystals of the same or different kinds, and nothing was said about the effect of inclusions, gas cavities, contraction cavities, &c. In this and the succeeding chapters, in which a closer approach to practice has to be achieved, no factor that has a bearing on the nature of metals or on the relations between this and treatment and properties can be neglected. Attention will therefore have to be given to a number of factors hitherto left out of account, and we shall have to show that metals as ordinarily prepared are much more complex materials than we have previously considered, and that the relations between nature, treatment, and properties are capable of almost infinite variations.

In Chapter I a metal was said to be defined in terms of its composition, constitution, microstructure, crystal structure, and condition. In Chapters II, V, and VI the constitution, microstructure, and crystal structure of metals and alloys were described, and although certain aspects of these will be considered more specifically in this and the following chapters there will be no new general features to introduce

except in so far as inclusions and cavities, being visible under the microscope, may be regarded as part of the microstructure. The additional aspects of the nature of metals that have yet to be considered come under composition and condition. It has been stated that treatment begins when a melt of the requisite composition has been prepared. Actually, however, metallurgists are not at present in a position to prepare melts containing so much of this and so much of that and nothing more. When all the available resources are utilized metals of very high purity can be prepared. Thus with zinc, silver, lead, gold, platinum, tin, and aluminium a purity of 99.99 per cent. has been substantially exceeded, and with copper and iron this purity has been almost reached. In general, however, metals of much lower purity have to be used, and when alloys are made by mixing metals containing impurities the total amount and the variety tend to increase. Thus although it is possible to produce alloys in which the amounts of the major constituents are controlled within close limits, a number of other elements will always be present in varying amounts and combinations. These elements are present either because it is technically impossible to remove them or because the advantages that would follow from their removal are not considered sufficient to warrant the expense involved.

In general, a metal or alloy may be said to consist of the basis metal (e.g. Cu, Al, or Fe) or the major constituents (e.g. Fe+C in steel or Cu+Zn in brass) and a number of minor constituents or impurities which (1) are associated with the basis metal in the ore and not subsequently eliminated, (2) picked up during the manufacturing operations, or (3) added to eliminate or counteract the effect of another element. If special efforts are made to detect every element in a given sample it will generally be found to contain a comparatively large number. As a rule, however, not all the elements present are determined, so that what is called the chemical analysis of a metal or alloy is usually only an approximation to the truth, and frequently a very rough one. Some minor constituents are known to be harmful, and others to be innocuous, but their significance varies according to the purpose for which the metal is intended, and amounts of impurities that have a serious effect on magnetic or electrical properties have no appreciable influence on mechanical properties. Frequently, however, the effect of the minor constituents is not known and is sometimes difficult to discover. To ascertain its effect it is necessary to have an alloy containing the basis metal, this particular impurity and nothing else. If this can be obtained the effect of the impurity can be determined. But in practice it will be present along with other impurities which may either accentuate or mitigate its effects, so that the complete investigation of the effect of impurities and the relations between them is an exceedingly laborious undertaking. At the present time a considerable amount of work is being done in order to discover the effect of minor constituents in metals and alloys, but we are a long way from being in a position to

state the precise effect of all the elements present in a sample of metal. In general, therefore, metals and alloys as prepared and used contain a number of elements that are not determined by analysis and the effects of which are not definitely known. Because of this the procedure during manufacturing operations may result in pronounced and puzzling alterations in the behaviour of a metal in service. Despite the work that has been done in the study of metals, a certain amount of mystery remains, in that the precise effect of a given procedure on the nature of the finished metal is not known, and the reasons why this procedure improves or impairs the behaviour of the metal in service have yet to be discovered. At the present time the problems that arise from this are receiving more attention than anything else in metallurgy, but until they are solved we have to content ourselves with the knowledge that if certain operations during manufacture are carried out in a certain way the finished metal gives better service than it otherwise would. In recent years a surprising number of mysteries have been cleared up, but many remain.

In previous chapters little has been said about the condition of metals. We have referred to the cast condition, the hot-worked condition, and the cold-worked condition, but these are distinguished from each other by differences in constitution and microstructure and can be described in terms of them. In stating that the nature of a metal is determined by the composition, constitution, microstructure, crystal structure, and condition it is implied that although all these attributes may be related, and although frequently it may be impossible to alter one without altering the others, each term should cover some characteristics of metals not capable of being included under the others. In this sense condition, although closely related to the other attributes, should signify some characteristic that cannot be said to be part of the microstructure, constitution, composition, or crystal structure. The most definite example of this is the degree of soundness. Metals as cast contain varying numbers of cavities of varying size and distribution which originate in several different ways. These determine its degree of soundness, and this varies considerably with the method of melting and casting. Some methods result in the formation of more cavities than others, but the composition of the molten metal as it leaves the furnace has a pronounced effect on soundness particularly in so far as this is connected with the evolution of gas. Thus soundness as a factor in condition is closely related to composition. Another factor is cleanliness, which is stated in terms of the amount of inclusions contained in the metal. As will be explained later, these are compounds of metallic and non-metallic elements (usually oxygen or sulphur) which have quite different properties from metals and exist as microscopically distinguishable constituents in the solid metal. Many of their effects on the properties of solid metals are incompletely understood, but they are generally considered to be detrimental. The amount and nature of

the inclusions present obviously depend to a marked extent on the composition of the molten metal, and except when they are too small they can be seen under the microscope, and may thus be regarded as part of the microstructure. Furthermore, the inclusions that exist as separate globules in the molten metal may have a pronounced effect on its solidification and thus affect both constitution and microstructure, and the same may be said of the effect of inclusions in the solid metal during crystallographic changes. Finally, condition may also be said to cover the state of the metal with regard to internal stress (Chapter X), or surface defects and internal cracks produced during hot- or cold-working or heat treatment.

MELTING

Many of the operations used in extracting metals from their ores are chemical or electrolytic processes which involve taking the metal into solution and depositing it again, but those most widely used involve melting. In this book we are not concerned with extraction and refining and the melting or other operations involved, but it is difficult to deal with casting and other treatments without saying something about earlier operations, and when these are introduced the problem is to know where to draw the line. For the present purpose it is convenient to confine the consideration of melting to the last operation of this sort that is performed before the metal is cast ready for service or subsequent treatment. The significance of this operation varies greatly, however, from metal to metal, and whereas on the one hand it may be a simple melting carried out in order to obtain the metal in a molten condition for casting, or to make up an alloy of specified composition, it may, on the other hand, be an essential part of the extraction and refining processes. For this reason it is necessary to consider briefly the position of the final melting-operations in the general scheme of the manufacture of metals and alloys. Attention may be given in the first place to the ferrous metals, and a simplified representation of the processes of ferrous metallurgy is given in Fig. 220. The first operation is the manufacture in the blast furnace of an iron alloy containing substantial amounts of carbon (generally about 3.5 per cent.), manganese, and silicon, together with varying amounts of sulphur and phosphorus. In terms of composition and constitution this alloy is cast iron, and it may be cast directly from the blast furnace into the shapes in which it will be used as shown at (1) Fig. 220. More usually, however, even when it is to be used as cast iron it is run from the blast furnace and allowed to solidify in blocks known as 'pigs' (2) Fig. 220; hence the name pig-iron applied to the product of the blast furnace whether solid or liquid. For grey iron castings the solid pigs are subsequently remelted (usually at a different plant) in a cupola, an air or reverberatory, an electric or a rotary-powdered-fuel-fired furnace as described in Chapter XIV. This ((3) Fig. 220) is the last melting operation

in so far as cast iron is concerned. It may involve simply the melting of pig-iron plus scrap cast iron, but in order to produce a cast iron differing substantially in composition from the product of the blast furnace the pig may be melted along with steel scrap and/or ferro-alloys, i.e. iron alloyed with high proportions of nickel, chromium, molybdenum, &c.

The characteristic of grey cast iron is that the composition is such that most of the carbon occurs in the solid iron as graphite, and the

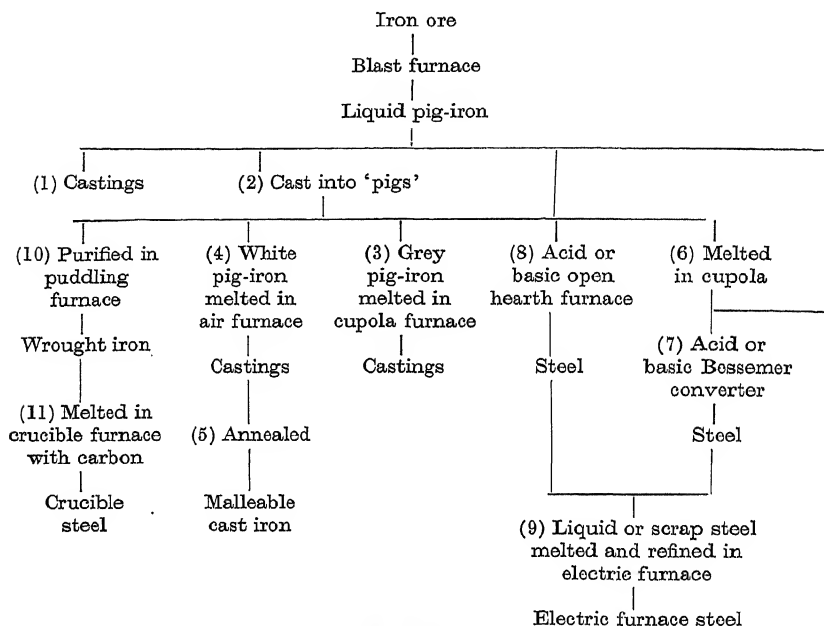


Fig. 220.

alloy is comparatively soft and easily machinable. In white cast iron, however, the composition is such that nearly all the carbon occurs as cementite, and the alloy is extremely hard and difficult to machine. For certain purposes white cast iron is used and is made by melting pigs of the requisite composition in reverberatory or electric furnaces ((4) Fig. 220). When malleable cast iron is required, white iron castings are annealed under conditions that remove some of the carbon and permit the remainder to change from cementite to graphite ((5) Fig. 220).

The iron produced in the blast furnace is the raw material used in making wrought iron and steel, both of which are produced by purifying the pig-iron. If this is low in phosphorus and sulphur, the object of the purification is to eliminate the carbon or to reduce it to the amount required in the steel. It is not in all cases necessary to eliminate the silicon and manganese, but there is no choice in the matter as these

are removed with the carbon. Purification depends on the fact that while the elements carbon, silicon, and manganese are soluble in molten iron their oxides are not. Furthermore, the affinity of these elements for oxygen is greater than that of iron. Consequently, if the molten pig-iron is oxidized, the elements carbon, silicon, and manganese are converted to oxides and eliminated from the melt. In the Bessemer process ((7) Fig. 220) this oxidation is carried out by blowing air through the molten metal, and the heat evolved in the oxidation of the impurities keeps the metal hot. As the Bessemer process must begin with molten metal the pig-iron must be taken direct from the blast furnace or previously melted in a cupola ((6) Fig. 220). In the open-hearth process solid pig and steel scrap or liquid pig and steel scrap are charged on to a shallow hearth and melted or maintained molten by burning producer gas over the surface of the metal. Oxidation is accomplished in the first instance by furnace gases, but once a slag has been formed on the surface of the metal these become less effective in this respect, and iron oxide is added from time to time to continue the oxidation.

The mechanism of oxidation is similar in the Bessemer and open-hearth processes. Oxygen from the air, furnace gases, or added oxide dissolves in the molten metal and there reacts with carbon, silicon, and manganese. The carbon is oxidized to carbon monoxide which escapes as bubbles, and these give rise to considerable agitation and cause the metal to boil. The oxides of manganese and silicon are formed as minute globules of liquid which have a lower specific gravity than the molten metal. These therefore move upwards through it, and as they rise increase in size by coalescence. This process involves not only the union of small globules of the same oxide, but also chemical combination between silica and manganese oxide to form a manganese silicate, between silica and iron oxide to form an iron silicate, and between manganese, silicon, and iron oxides to form an iron-manganese silicate. Finally, the globules rising out of the metal collect on the surface and there form a slag which is an iron-manganese silicate. As in all other metallurgical operations, the amount of oxygen that must be taken up by the molten metal is considerably in excess of that required to combine with the elements being eliminated, so that, while elimination is going on and after it is completed a certain amount of oxygen remains dissolved in the metal as iron-oxide.

The manufacture of steel from pig-iron of low phosphorus content is carried out in Bessemer or open-hearth furnaces lined with refractory materials which consist essentially of silica. There is therefore little reaction between the furnace lining and the silicate slag. When the pig-iron contains a high proportion of phosphorus this must be eliminated in steel-making, but although it is oxidized with the other elements it is not retained in a silicate slag and therefore passes back into the metal. In order to remove the phosphorus the slag must be rich in

lime, and such a slag may be produced by adding a suitable quantity of lime to the furnace charge. When this is done, however, a siliceous lining cannot be employed, for there would then be a rapid reaction between it and the slag. When, therefore, a limey slag is to be formed a lining that does not react with it must be provided, and for this purpose linings of magnesia (MgO) or calcined dolomite (MgO , CaO) are usually employed. Now the phosphorus content of pig-iron depends on that of the ore from which the iron is made, and this fact gives rise to the division of steel-making processes into two groups. If the ore is low in phosphorus the pig-iron is low in it, and the steel can be made in a furnace lined with silica and without addition of lime. As slags and refractory materials rich in silica are called acid, processes of this kind are known as acid processes. If, however, the ore is high in phosphorus the pig-iron made from it is high in this element, and to eliminate it the steel must be made in a furnace lined with metallic oxides so that a limey slag may be produced. Slags and refractory materials rich in metallic oxides are called basic, and hence processes of this kind are known as basic processes. Thus steel may be made either by the acid or basic Bessemer process ((7) Fig. 220) or the acid or basic open-hearth processes ((8) Fig. 220).

When the manganese, silicon, and phosphorus have been removed and the carbon eliminated or reduced to the amount required in the steel a certain amount of iron-oxide remains in solution. If the carbon has been taken out or reduced below the amount required in the steel some must be added to obtain the correct composition, and consequently the finished steel contains both carbon and iron-oxide. So long as these constituents are present together they tend to react to form carbon-monoxide gas. If this reaction is going on while the steel is solidifying after being run into moulds, a certain number of gas bubbles will be retained in the steel as blowholes. Actually, if nothing is done to prevent it, the evolution of gas during solidification will result in a steel that is honeycombed with blowholes. To prevent this the steel must be wholly or partly deoxidized, and this is done by adding manganese, silicon, and aluminium. These elements have a greater affinity for oxygen than the carbon, and consequently liquid oxide globules are formed instead of gas bubbles. These tend to rise out of the steel, to coalesce and unite in the same way as the globules formed during the purification stage. The extent to which they will rise out of the metal depends on the time that is allowed to elapse between the addition of the manganese, silicon, and aluminium and the solidification of the steel. Such globules as have not risen to the surface before solidification occurs are trapped in the solid steel as inclusions of aluminium, manganese, or silicon oxides or varying combinations of these and iron oxide in the form of silicates.

In the Bessemer and open-hearth processes the means of oxidation and the means of heating are practically the same, and it is impossible

to keep the metal hot without oxidizing it. Consequently, the metal cannot be kept molten after the addition of the deoxidizers in order to allow the oxides and silicates thus formed to rise to the surface. For steels of ordinary quality the Bessemer or open-hearth process is the last melting-operation, and the resulting steels contain varying but considerable amounts of inclusions. For steels of special quality, however, another operation is performed in an electric furnace ((9) Fig. 220) of the arc or high-frequency induction type. The charge for these furnaces may be molten steel from one of the other furnaces or steel scrap, and the object of this extra operation is to refine the steel under conditions which permit separate control of heating and oxidation. In such furnaces slags of any desired composition may be produced, phosphorus and sulphur eliminated, and inclusions given an opportunity to rise out of the metal.

The manufacture of wrought iron ((10) Fig. 220) resembles that of steel by the basic open-hearth process in that the pig-iron is melted on a shallow hearth lined with metallic oxide (iron oxide in this case) and heated (and oxidized) by a flame passing over the surface of the metal. As the impurities are eliminated, however, the melting-point of the metal rises, mainly as a result of the removal of carbon (see Fig. 272) and the metal becomes pasty in the furnace. The pasty metal and slag are rolled into balls in the furnace, hammered to squeeze out as much slag as possible and then rolled. The characteristic of wrought iron is that it contains considerable quantities of slag which gives it a kind of laminated structure when rolled. Crucible steel ((11) Fig. 220) is made from wrought iron of high quality by melting it in small pots and adding pig-iron of high purity or anthracite to supply the carbon required in the steel.

When steels other than plain carbon steels are required the other elements such as nickel, chromium, molybdenum, tungsten, &c., are added in the form of ferro-alloys during one of the processes described above. Alloy steels are not made by the Bessemer process, but several types such as high-tensile structural steels, and general-purposes alloy steels, i.e. steels of low or medium alloy contents, are made by the open-hearth process. Steels of high alloy content such as stainless, high-speed, and magnet steels are made in electric furnaces, and when the highest quality is required other alloy steels and even carbon steels are made in this way.

In non-ferrous metallurgy the arrangement of the operations is quite different. In the first place there is a series of extraction and refining processes designed to produce the individual metals in different degrees of purity. Alloys are made by melting and mixing metals in appropriate proportions, and finally castings and ingots for subsequent treatment are frequently made by remelting previously prepared alloys. Thus copper or aluminium at the end of the manufacturing processes may be cast into ingots which may then be rolled into rod or sheet or

remelted with other metals to make alloys. These alloys, when made, may be cast directly into the form in which they will be used or into ingots for rolling. Alternatively, they may be cast into ingots that are subsequently remelted, and then cast into the form in which they will be used. Besides the virgin metals obtained by extraction and refining, scrap metals are also used in making alloys. These may be mixed with virgin metals and melted when the alloy is being finally prepared. Alternatively, they may be melted and cast into ingots which are remelted along with virgin metals. In the manufacture of brass or bronze the copper is melted and zinc or tin is added, but in the manufacture of other alloys, and in adding other elements to brass and bronze, intermediate alloys comparable with the ferro-alloys used in steel making are employed. Thus in making aluminium-copper alloys an alloy containing 50 per cent. of each element is made up and then added in suitable amounts to molten aluminium to make alloys containing 4, 8, or 12 per cent. of copper. These intermediate alloys are known as hardeners and their manufacture is a definite branch of the non-ferrous industry. For the addition of other elements to aluminium, hardeners consisting of aluminium plus 15 or 30 per cent. of silicon, 10 per cent. of nickel, 10 per cent. of manganese, or 10 per cent. of iron are made, and for the addition of other elements to copper, hardeners consisting of copper plus 10 or 15 per cent. of phosphorus, 50 per cent. of nickel, 25 per cent. of manganese, or 10 per cent. of silicon are made.

The complicated system of melting-operations in non-ferrous metallurgy arises partly from technical considerations and partly from the organization of the industry. The extraction and refining of the basis metals is carried out by comparatively large concerns which may or may not produce rolled, drawn, and extruded articles from these metals. In any case they also provide ingots of varying sizes and shapes for others who roll, draw, and extrude them, melt them with other metals and scrap to make alloys, and either cast and work these alloys or sell them to the concerns where the alloys are melted again, cast and worked. As an example of the complications that may be introduced for technical reasons the following instructions given for the manufacture of a special brass may be quoted (236). [The brass in question is to contain aluminium, iron, manganese, and nickel in addition to copper and zinc. First the special elements are alloyed with a certain amount of copper and cast into bars to form an intermediate alloy. The remainder of the copper is then melted, and the necessary amount of zinc and intermediate alloy added. This is then cast into ingots which are remelted and cast into moulds to give the finished product. This technique is employed to overcome certain difficulties encountered in the manufacture of complex brasses. During the first melting of the intermediate alloy a certain amount of gas is absorbed. This, however, is mostly eliminated during the second melting when the high zinc content protects the melt against excessive gas absorption. Aluminium, manganese, iron, and

nickel are readily oxidized, and if the alloy were cast into moulds after the first remelting many oxide inclusions would be formed. After casting into ingots and remelting, these defects are practically eliminated, and a sound casting is obtained.

For the purpose of a general consideration of melting and casting it is inconvenient and unnecessary to endeavour to cover all the types of melting operations that may be performed in the non-ferrous industry, and attention will be confined to the final melting of copper, the melting of brass and bronze, and the melting of aluminium alloys. The final melting in the manufacture of copper is an important part of the refining process and is described in Chapter XV. The final melting of aluminium is also the main extraction process whereby the metal is obtained from alumina and is described in Chapter XVI. Copper and aluminium alloys are made by melting the basis metal and adding the other constituents either as metals or in the form of intermediate alloys.

The object of the final melting-operations in ferrous and non-ferrous metallurgy is to produce a melt of the required composition, and what we are concerned with in this chapter is the extent to which this can be done and the extent to which the meaning of a melt of the required composition is understood. Sometimes the production of such a melt involves producing a substantial alteration in the basic raw materials charged, by eliminating impurities, as in the manufacture of steel or the refining of copper, or by adding other elements, as in the manufacture of alloy steels and non-ferrous alloys. Sometimes, however, it simply involves preventing any change in the basic raw materials, as in the melting of previously prepared alloys for casting purposes. In either case the factors that have to be taken into account are the basic raw materials charged, the additions (if any) made, the reactions between the molten metal and the furnace atmosphere and the reactions with the furnace lining. If some purification has to be carried out, reactions between the metal and the furnace gases will be promoted as in the manufacture of steel or the fire-refining of copper. But in order that the reactions may accomplish the desired result they must be promoted to excess, and consequently the elimination of the original impurities results in the introduction of a new impurity which in turn must be eliminated. If no change in composition is required then reactions between the molten metal and the furnace or its atmosphere must be prevented as far as possible, but as these can rarely be prevented completely some additions must frequently be made to counteract their effects.

The actual casting process has a pronounced effect on the condition of the metal as cast, but in so far as the nature of the casting is influenced by the composition of the melt three different features may be recognized: (1) the alloy proper, (2) the inclusions, and (3) the gases. In previous chapters attention has been confined almost entirely to

the alloy proper which consists of crystals of primary solid solutions and intermediate constituents arranged in various ways. The first characteristic to be noted about inclusions is that they are compounds of metallic and non-metallic elements which exist as distinct constituents in the solid metal. They are frequently called non-metallic inclusions, but as the term inclusions is not applied to any constituents except those in which one of the elements is a non-metal it is unnecessary to use the full designation. Some intermediate constituents, however, are also compounds of metals and non-metals, e.g. iron carbide, magnesium silicide, and copper phosphide, and these are regarded as belonging to the alloy proper. In order to distinguish inclusions from such intermediate constituents, the definition given above must be extended so as to limit inclusions to compounds that are known or considered to have a deleterious effect on the alloy, and which would be eliminated if possible. They are mainly oxides, silicates, sulphides, and more rarely nitrides and carbides. The most characteristic inclusions are those which exist as distinct liquid globules or solid particles distributed throughout the molten metal. Examples of this kind of inclusions are provided by the globules of oxides and silicates that exist in molten steel after the deoxidizers have been added, and which are subsequently entrapped to varying extents in the solid metal. Other constituents classified as inclusions are, however, soluble in the molten metal and only become distinct constituents when solidification occurs. Examples of this type are provided by oxide inclusions in copper, iron sulphide inclusions in steel, nickel sulphide in nickel, and iron phosphide inclusions in cast iron. A third type of inclusions which differs entirely from any of those described above, in that their formation has nothing to do with the reactions in the molten metal, are the particles of furnace, ladle, and mould-lining that may be detached and solidified in the metal.

From the point of view of the condition of the metal as cast, the important aspect of the relations between gases and metals is the evolution of gas during solidification. As will be explained later, this is only one of several aspects of these relations, for in addition to the effects of gases on solid metals described in Chapter VIII reactions between gases and liquid metals may lead to the formation of inclusions or changes in the alloy proper. From the point of view of the cast condition, however, it is not with the reactions between gases and metals that we are concerned but the evolution of gas from metals. These factors are usually related but not necessarily so. Molten metals have a greater solubility for gas than solid metals, and consequently if a gas is dissolved in a molten metal and does not form a non-gaseous compound with it (or with some other constituent) it will be evolved as the metal solidifies. Hydrogen is thus picked up and evolved by aluminium and its alloys. More usually, however, the evolution of gas during solidification is due to a reaction taking place in the metal. Thus the

principal gas evolved from steel is carbon monoxide produced by a reaction between carbon and iron oxide, and the principal gas evolved from copper is steam produced by a reaction between hydrogen and copper oxide.

The general object of the final operation is to produce a melt of such a composition that the alloy proper will contain a minimum of undesirable impurities, that the amount of inclusions will be small, and that the gas evolved at solidification will be negligible or under control. In attaining this object the metallurgist has to decide on the type of furnace to use and the atmosphere that can be maintained in it, he has to select his raw materials, make his additions to the metal or the slag, and generally conduct the melting operation so as to obtain the best results according to his knowledge. To some extent the control of melting means control of the actual composition of the melt in terms of the elements present, but it also means control of the condition in which these elements are present. Thus it is said that manganese, silicon, and aluminium are added to steel to deoxidize it, whereas in point of fact they simply convert iron oxide which will react with carbon into other oxides which will not, and thus prevent the evolution of gas without necessarily decreasing the amount of oxygen in the steel. Similarly, manganese is added to steel to convert iron sulphide, which is soluble in the molten but not in the solid steel, into manganese sulphide which is not soluble in the molten steel.

THE CASTING PROCESS

The operation of pouring a molten metal into a mould in which it solidifies is known as casting. As the processes of extraction and refining of metals usually finish with the metal in the molten state almost all metals must be allowed to solidify in some kind of mould. There are, however, several exceptions to this practice. Wrought iron, e.g., exists in the form of a pasty mass at the end of the manufacturing process and consequently cannot be cast. It is worked into balls in the furnace and is then hammered and rolled to shape. The high-melting metals tungsten and molybdenum are not melted in the process of manufacture. They are obtained in the form of powder by the reduction of their oxides, and by the application of heat and mechanical force the particles are fritted together to form rods. Again, those metals that are extracted or refined electrolytically, or by wet chemical methods, are not in a molten state at the end of the manufacturing operations, but as the form and condition in which they are obtained in such processes are generally unsuitable for service purposes, or for further treatment, the metals produced in this way are subsequently melted and cast.

Apart from the necessity of casting metals which are produced in a molten state the operation is a convenient way of obtaining solid masses of suitable size and shape. If the metal is cast in the form in which it will be used the solid mass is known as a casting; if it is cast into a

simple shape for subsequent working it is known as an ingot or a slab, cake, or wire-bar. Large quantities of metal go into service just as they are cast or after annealing to remove casting stresses. Cast iron, which cannot be shaped by hot- or cold-working, is always used in the form of castings, and the same applies to most bronzes and aluminium-copper alloys containing 6 per cent. of copper or more. As just stated wrought iron, tungsten, and molybdenum cannot be cast, but most metals, e.g. steel; copper, brass, aluminium alloys other than those of high copper content, lead, nickel, zinc, tin, magnesium, and their alloys may be used either cast or worked.

The conditions under which casting is carried out have a pronounced influence on the properties of the metal even when it is subsequently worked. The phenomena associated with casting are therefore amongst the most important involved in metallurgy. Providing that a suitable mould material is available, and that the metal can be made sufficiently fluid all properly designed moulds may be filled with molten metal. But this does not ensure that a successful casting will result, and great care and skill are required in order to produce castings free from cavities, cracks, and surface imperfections. The responsibility for successful casting is shared by the designers, pattern-makers, moulders, and the men who melt and pour the metal, and the best results are obtained when there is proper co-ordination between them. As this book is mainly concerned with the phenomena exhibited by metals, the technique of foundry practice does not come within its scope. In what follows, attention will therefore be directed rather to the behaviour of the metals than to the ingenuity and skill displayed by those who cast them.

The moulds into which metals are cast are divided into two main types, viz. sand moulds and metal moulds, which give rise to two different systems of casting and two different kinds of castings. The principal differences between these are that (1) metal moulds are permanent and can be used for numerous castings, whereas a new sand mould must be made each time, and (2) the rate of cooling in metal moulds is more rapid than in sand moulds. But whichever type of mould is used it must stand up to the hot metal flowing into it. From sand moulds heat is only dissipated slowly because of the comparatively large mass of sand which surrounds the molten metal, and the inner surface of the mould is heated to a temperature approaching that of the melt. To resist this, refractory sands are used. The resistance of metal moulds does not depend so much on their refractoriness, as on their high conductivity for heat. As a result of their rapid abstraction of heat, a layer of the incoming metal is 'chilled' on to the inner surface of the mould which is not heated to a temperature approaching that of the melted metal.

Moulds must be constructed to allow for the escape of the air displaced by the metal, and of the gases liberated from the metal, the mould, or

the mould dressing. Most metals evolve gas when they are solidifying, and the moisture which is usually present in sand moulds is converted into steam by the hot metal. Frequently also, the inner surface of moulds is dressed with a coating of material which is volatilized by the hot metal and gives rise to reducing-gases which prevent its oxidation. An essential feature of moulding sands is therefore their porosity which allows gases to escape instead of being entrapped between the metal and the mould, and this natural porosity is usually supplemented by 'venting', i.e. by making narrow holes that extend from the outside of the mould to within a short distance of the inner surface. Metal moulds are not gas porous, but many of them are open at the top and the gases escape from there. As no gas is liberated from metal moulds, however, castings may be made in closed moulds if the metal being cast is thoroughly degasified. If this is either impossible or inconvenient vent-holes may be made in the mould. As all metals contract while they are cooling from the casting-temperature to the freezing-point, and as most of them also contract on solidification, provision must be made for the constant addition of fluid metal in order that the solid casting may fill the mould. This is known as feeding.

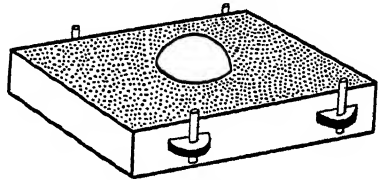


FIG. 221.

Sand Moulds.

The first stage in making a sand casting is the preparation of the pattern. This is a wooden or metal replica of the article required, but is slightly larger to allow for the contraction of the metal during cooling from the temperature of solidification to that of the atmosphere. The sand is rammed round the pattern so that a hole is formed in it of the same shape as the pattern. The fact that the pattern must then be withdrawn without disturbing the mould introduces a number of complications into the operation. It would clearly be impossible to withdraw the pattern from the interior of a mass of sand without destroying the shape of the latter. Consequently, moulds are made in two halves. In the first place the pattern is sunk half-way into the sand contained in a moulding frame, which is simply a suitably shaped iron box without top or bottom. The sand is rammed, levelled, and dusted over with a parting medium consisting of burnt sand. In this way the stage shown in Fig. 221 is reached. Another frame which is fitted with lugs drilled with holes that fit over the pins on the bottom frame, is then placed over the first and filled with sand. A round feeding-peg is placed on the top of the pattern and a round runner-peg at a short distance from it. The top half of the frame is now rammed with sand, and the pegs withdrawn. Finally, the two halves of the mould are separated, the pattern taken out, and a small channel (or gate) cut in

the lower half of the mould to connect the impression of the pattern with the bottom of the hole left by the runner-peg. When the two halves of the mould are placed together again the section through the mould is as shown in Fig. 222. The mould is filled with molten metal poured through the runner-hole *R*, until it rises to the top of the riser or feeding-hole *F*. As the liquid contracts, the level of metal in the feeding-hole sinks, and if necessary more liquid may be added at *F* to ensure an adequate supply to the mould.

Making a pattern and mould for casting a solid sphere or other simple shape is comparatively easy, because there is no difficulty in withdrawing the pattern. But making the moulds for more complicated shapes is a skilled operation, and considerable ingenuity is displayed in designing the patterns so that they may be taken to pieces for removal.

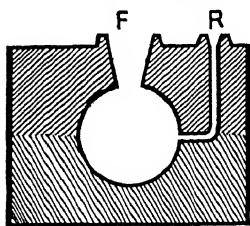


FIG. 222.

When hollow castings are required, 'cores' are used to fill the internal spaces. These are sand impressions of the internal form of the casting. The patterns for the cores are known as core boxes. They are made in two halves which are placed together and rammed with sand. The halves are then separated, and the sand core removed from the box, dried in a stove, and finally placed in the required position in the mould.

Moulding sands must be sufficiently refractory to withstand the temperature of the molten metal. They must also be porous and possess sufficient cohesion to retain the shape into which they are pressed. The refractory quality of such sands is conferred on them by their contents of silica and alumina. Most sands contain over 90 per cent. of silica associated with from 5 to 8 per cent. of alumina. The cohesive quality depends on the presence of clayey matter. The higher the content of this the stronger is the sand, but there is a limit to the amount of clay permissible for it tends to destroy the porosity. All sands are worked in a moistened condition such that when a handful is squeezed it retains the shape impressed on it, but does not stick to the hand. Sometimes the metal is cast in the moulds just as they are made. This is known as 'green sand' casting. When the moulds are dried in a stove before being used they are known as 'dry sand' moulds. Cores are nearly always stove-dried to increase the cohesion of the sand and facilitate handling as well as to increase their porosity.

Ingot Moulds.

Sand casting is the usual method of producing castings to be used as such, but metal moulds are almost exclusively employed in casting metals for subsequent mechanical working, i.e. in casting 'ingots'. For this purpose relatively simple shapes, which vary in form and dimensions according to the purpose for which they are to be used, are cast.

Cast iron is generally used for ingot moulds, but steel is also employed, and the use of solid or water-cooled copper moulds for ingots of aluminium and copper alloys has been considerably extended in recent years. These ingot moulds are always open at the top so that gases may easily escape. Usually they are filled by pouring the liquid metal from the top, but for special purposes bottom running is used. In this case the liquid metal is poured down a funnel which is connected by runners to the bottom of one, two, four, or even eight ingot moulds. Primarily, the function of ingot moulds is to provide a receptacle in which the liquid metal shall solidify in a form suitable for subsequent working. But in addition to this they must abstract heat from the metal and dissipate it from their outer surface. As the mould is at a much lower temperature than the metal poured into it, a layer of the melt is immediately chilled on to its inner surface. When plain steel or cast-iron moulds are used, this effect increases with the thickness of the mould, but in water-cooled moulds it increases as the metal thickness decreases, for in these the chill is due to heat removed by the circulating water behind the surface in contact with the molten metal. The proportion of the ingot that is affected by the chilling action of the metal moulds depends on the relation between the mass of the ingot and that of the mould. If the mass of the latter is sufficiently great the chilling action may persist throughout the whole process of solidification. This frequently occurs when small ingots are being cast, and it is with a view to increasing the depth of the chill that water-cooled moulds have been introduced. When large ingots are cast, however, the chill effect is exhausted by the time a thin layer of metal has solidified. Thereafter, the mould is maintained at a comparatively high temperature, and the cooling of the melt depends on the conduction of heat through the solid metal and the mould, and the loss by radiation and convection from the outer surface of the mould.

Permanent Mould or Die-casting.

The production of castings other than ingots in permanent metal-moulds has become an important industry during the last twenty years. Sand castings must always be machined in order to obtain a satisfactory surface or accurate dimensions, and owing to the necessity of making a new mould for each casting, the process is discontinuous. These difficulties may be overcome by casting in metal moulds, but other difficulties arise which limit the applications of such methods.

Three different processes are employed in making castings in metal moulds: (1) pressure die-casting, in which the liquid metal is forced into the mould under pressure, (2) permanent mould or gravity die-casting in which the metal is poured into the mould as in sand-casting, and (3) centrifugal-casting, in which the molten metal is run into a rapidly rotating mould and forced up the sides by centrifugal force to form a hollow cylinder. Each of these methods has its particular advantages

and disadvantages, and in comparing them with each other and with sand-casting numerous factors must be taken into account.

A pressure die-casting may be described as a finished casting made by forcing a liquid metal under pressure into a permanent metal mould. Owing to the smooth surface obtained, no machining other than that involved in removing fins and making holes for screws and bolts is required to prepare the casting for service. Once the necessary dies have been designed and prepared, castings can be produced at a rapid rate and within close dimensional tolerances. Castings of very thin and light sections can be made, and engraved and ornamental designs can be accurately reproduced. The process was first applied to alloys of low melting-point consisting essentially of tin, tin and lead, or zinc. It was then extended to aluminium alloys and later to aluminium-bronze and finally to brass. The manufacture of brass pressure die-castings has been gradually developing since about 1932, and now the process is being applied to cast iron. A large number of alloys based on the metals mentioned are used for pressure die-casting, and these are considered in more detail in Part VI. Meanwhile, a few of the most widely used alloys may be mentioned. In the tin-lead series the tin content varies from 75 to 25 per cent. while the lead content varies from 8 to 56 per cent., and copper and antimony are generally present in the proportion of 4 and 13 per cent. respectively. A number of zinc-tin alloys containing from 70 to 90 per cent. of zinc and 5 to 25 per cent. of tin with the addition of 3 to 4 per cent. of copper are used, but in so far as zinc-base alloys are concerned the best results appear to be obtained with zinc-aluminium alloys containing 3.5 to 5 per cent. of the latter element, 0.02 to 0.1 per cent. of magnesium, and with or without 2 to 4 per cent. of copper. Many aluminium-base alloys are used for die-casting, but those most widely employed are aluminium plus 8 or 12 per cent. of copper, aluminium plus 5 or 12 per cent. of silicon, and several more complex alloys containing both copper and silicon and sometimes nickel. Of the brasses, those most suitable are the α + β alloys (about 60 Cu, 40 Zn) which have a lower melting-point than the α alloys (about 70 Cu, 30 Zn). Usually some of the zinc is replaced by other elements, and a typical composition is copper 60 per cent., lead 1 per cent., tin 1 per cent., aluminium 0.1 per cent., and the remainder zinc. Most pressure die-castings are comparatively small, and the upper limit for castings made from the most extensively used alloys, i.e. aluminium or zinc base, is about 16 lb. weight.

Pressure die-castings are produced in specially constructed machines of which several types have been devised. The essential features are a melting-pot in which the alloy is kept molten, a device for forcing the liquid alloy into the mould, and the die or mould together with the necessary mechanism for opening and closing it and for ejecting the solid casting. Two methods are used for forcing the metal into the die, namely, by using a piston or by air pressure. The minimum pressure is

about 100 lb. per sq. in., and it increases with the size and intricacy of the casting. In some methods of die-casting brass the metal is not forced into the mould when in a liquid condition. It is maintained at a temperature between the liquidus and solidus and is forced into the die in a 'mushy' condition. For this purpose pressures of about 2.5 tons per sq. in. are sometimes used.

The metal dies are subjected to exacting conditions and the problem of maintaining them is an important one which becomes more difficult to solve as the melting-point of the alloy increases. For casting zinc-, tin-, and lead-base alloys, dies of plain carbon steel (0.2–0.5 per cent. carbon) or of nickel-chromium steel (0.4–0.5 per cent. carbon, 0.75–0.9 per cent. chromium, and 1–1.5 per cent. nickel) are used without heat treatment. For aluminium- and magnesium-base alloys a chromium-vanadium steel (2–2.5 per cent. of chromium, 0.15–0.3 per cent. vanadium) or a chromium-tungsten steel (4.75–5.75 per cent. chromium, 4.0–5.0 per cent. tungsten) is used in the hardened and tempered condition. The last steel mentioned may also be used for copper-base alloys or as an alternative, one containing 2.75–3.5 per cent. of chromium and 8.5–10.5 per cent. of tungsten may be employed. This steel is also hardened and tempered. In the recently introduced process of pressure die-casting cast iron, cheap and easily replaceable dies are used instead of endeavouring to provide a material that will stand up for a considerable time. Thus dies made of cast iron faced with mild-steel sheet are used.

The design of dies is a very important aspect of the process. They must allow free access of metal to every part of the mould, the cores must be carried by the dies, and the whole must divide into two parts to permit the easy and rapid ejection of the casting. Furthermore, the dies must be made with great accuracy, and their preparation is therefore expensive. Consequently, it is not economical to make die-casting except when a large number of similar pieces is required. On account of the pressure employed, adequate venting is impossible, and thus air and gas evolved from the metal are entrapped in the castings. The process operates most satisfactorily when the dies are hot, and they are maintained in this condition by the molten metal.

The chief disadvantage of the process is the porosity resulting from entrapped air and evolved gases, and for this reason they should not be used when strength or resistance to fluid pressure is important. When products that require the advantages without the disadvantages of pressure die-castings are wanted, the gravity method is used. This resembles the process just described in that the castings are made in permanent metal moulds and have a good surface and accurate dimensions. But the moulds are assembled, filled, and taken apart by hand, and the rate of production is therefore much slower. Gravity die-casting is not used for tin-, lead-, and zinc-base alloys, but it has been in use for many years for aluminium- and copper-base alloys and cast iron. Proper

venting can be arranged and castings free from porosity produced. The principal use of the centrifugal-casting process is in the manufacture of cast-iron pipes, but it is also employed in making other cast iron and bronze products where hollow cylinders are required, e.g. cylinder liners, piston rings, and bronze gear-blanks. In this process the mould or die is a steel cylinder which is rotated at a rate of 300–1,200 revolutions per minute about a horizontal or a slightly inclined axis. Molten metal is poured along the lower inside surface of the cylinder and is spread round its inner surface during rotation.

PHENOMENA ASSOCIATED WITH CASTING

The Evolution of Gas.

Gas cavities (blowholes) in cast metals may arise in four ways: (1) from air in the mould being entrapped by the metal, (2) from the gases produced by a volatile mould dressing, (3) from steam generated by evaporation of moisture from the mould surface, and (4) from gases evolved from the solidifying metal. In sand-casting the porosity of the sand, the vents and the risers, facilitate the escape of air and gases generated at the metal-mould surface, and gases produced by volatile dressings can be prevented by adopting other methods of avoiding oxidation during casting when this is necessary. In casting ingots the escape of air and the gas (if any) generated by the mould dressing is facilitated by the open top, and in gravity die-casting the same result is obtained by the use of risers and vents. Dies used for pressure die-casting do not make much allowance for the escape of air, and the entrapping of this is a characteristic of the process. In all casting processes, however, it is difficult to provide for the escape of gases evolved from the solidifying metal, and this is one of the most important of the problems associated with casting.

The evolution of gases from solidifying metals is just one aspect of the general relations between gases and metals. In Chapter VIII several aspects are described, and in an earlier section of this chapter the use of gases for purifying metals and the contaminating effect of gases are considered briefly. These aspects of the relations between gases and metals cannot be completely dissociated from the phenomena now under consideration and will have to be referred to in this section. Attention will principally be directed, however, to the liberation of gas during solidification, and the other aspects will only be considered as far as they bear on the origin of the gas thus liberated.

One of the principal factors influencing the liberation of gas during freezing is the fact that gases are more soluble in liquid than in solid metals, and consequently if the liquid contains more gas than is soluble in the solid this will be liberated. The gas so liberated may have been present in cavities or in enforced solution in the scrap or virgin metal melted, e.g. hydrogen in electro-deposited copper. It may have been absorbed directly from the atmosphere during melting as when

silver dissolves oxygen, or it may have been picked up through the molten metal dissociating a compound gas, as when aluminium dissociates water vapour to form aluminium oxide and hydrogen which dissolves in the metal. The other principal cause of the liberation of gas is its formation by a reaction taking place during solidification. In this case neither of the reactants may be gases, as when carbon monoxide is produced in solidifying steel by a reaction between carbon and iron oxide, or one of them may be a gas, as when steam is produced in solidifying copper by a reaction between hydrogen and copper oxide. Whatever its origin the liberated gas may escape from the metal prior to or during solidification by diffusion or in the form of bubbles, or it may be retained in the solid metal in blowholes or pinholes which are actually entrapped bubbles. In considering the phenomenon attention must therefore be given to (1) the origin of the gas or the constituents that react to form gas, (2) the factors that affect the liberation of dissolved gas or the reactions that produce gas, (3) the factors that promote bubble formation, and (4) the conditions under which bubbles escape from or are entrapped in the metal.

On the one hand, in so far as the properties of the cast metal are concerned, gas cavities have a detrimental effect and have to be avoided as far as possible. On the other hand the entrapping of gas bubbles results in an increase in the volume occupied by the solid metal and, by compensating for the contraction that normally takes place at solidification, assists in producing castings that fill the mould. Furthermore, in certain cases, gas cavities, that are not so near the surface as to be exposed to the air during working, are welded up during this operation and have little effect on the properties of the finished metal. In view of these facts it is not necessary or even desirable to eliminate gas in all cases, and while the object of melting and casting technique is sometimes to eliminate gas, at other times it is simply to control the amount, size, or distribution of the cavities.

The Condition of Gases in Metals.

In considering the condition in which gases can exist in metals, some confusion is liable to arise if care is not taken to distinguish between the presence in metals of elements that normally exist as a gas and the presence of actual gas. If this distinction is not made and gases are considered to be elements normally occurring as gases, e.g. oxygen, hydrogen, and nitrogen, then gas may be said to exist in solid metals in three forms (in addition to adsorbed layers): (1) in chemical combination with the basis metal or some other constituent, (2) dissolved in solution as a gas, or (3) in blowholes. Gaseous elements in chemical combination with the basis metal or other constituent are not present as gas unless the resulting compound is gaseous. Oxygen in steel and copper, for example, is present mainly as iron and copper oxides and these are not gases, but it may also be present in blowholes

as carbon monoxide or steam and these are gases. Similarly, nitrogen is generally present in steel as a nitride and this is not a gas. When, therefore, a distinction is made between gaseous elements present in one form or another and actual gases it may be said that the latter may exist in two conditions, viz. in solution in the metal or in blowholes.

When a gaseous element forms compounds with a metal, the relations between the two elements may be represented by an equilibrium diagram such as that for the copper-oxygen system described in Chapter XV. According to this system oxygen is soluble in solid copper to the extent of 0.0156 per cent. (i.e. 10.9 c.c. of oxygen per 100 gm. of copper) at 1,050° C., and to the extent of 0.0071 per cent. (5 c.c. per 100 gm.) at 600° C. This amount of oxygen may be considered to exist as a gas in solid copper, but any excess of oxygen exists as microscopically distinguishable particles of copper oxide. Similar conditions are realized with iron and oxygen. Here oxygen is soluble in the solid metal to the extent of from 0.1 to 0.2 per cent. at the temperature of the eutectic, and the solubility changes with temperature and with the polymorphic changes in the iron. Again, the amount of oxygen soluble in the metal may be said to be present as a gas while any excess is present as the oxide. Finally, similar conditions are again obtained in the system iron-nitrogen, where iron dissolves 0.13 per cent. of nitrogen as a gas and any excess occurs as plates of iron-nitride (Fe_4N), and also in the systems molybdenum-nitrogen, chromium-nitrogen, nickel-oxygen, &c.

In systems of the types described above, the oxygen or nitrogen in solid solution and the oxides and nitrides existing as separate constituents may arise from the solidification of melts containing these gases in solution. Alternatively, the same conditions may be produced by heating the solid metals in the gases under such conditions that gas diffuses into the metal. Then oxygen, for example, will form a solid solution until the limit of solid solubility is reached and thereafter oxide will begin to form. There are no experimental methods of determining whether oxygen or nitrogen exist in molten metals as gases or as oxides and nitrides. To preserve the analogy between these and other alloys it might be assumed that they are present as dissolved gases. It is customary, however, to suppose that these gases exist in the liquid metals as oxides and nitrides and this practice may be adhered to. In the case of hydrogen which does not form compounds with the solid metals it is customary to regard it as being dissolved in molten metals as a gas.

From the point of view of this chapter three different aspects of the relations between gases and metals may be recognized, namely (1) gases with which metals come into contact, (2) gases present in metals, and (3) gases extracted from metals. The relations between these are rather complicated and liable to lead to confusion unless carefully considered. We have already seen that the gases with which liquid metals come into contact may (1) dissolve, as when hydrogen produced by the dissociation of water vapour dissolves in iron, copper, or aluminium,

(2) form a soluble compound with the basis metal or some other constituent as in the case of iron oxide in steel, (3) form a liquid or solid insoluble compound with the basis metal (e.g. aluminium oxide in aluminium) or some other constituent (e.g. manganese oxide in steel), or (4) form a gaseous insoluble compound as when carbon monoxide is formed in steel. Of these four alternatives only (1) and (4) lead to the presence of gas as such in the metal, (1) gives rise to dissolved gas and (4) to gas in the form of bubbles. When the liquid metal solidifies, some of the dissolved gas will escape, some will be entrapped in blowholes, and some may remain in solution in the solid metal. In addition to this, however, reactions between constituents may result in the formation of insoluble gases, e.g. carbon and iron oxide in steel and hydrogen and copper oxide in copper, and these will also be entrapped in the blowholes. When, therefore, gases are extracted from solid metals several gases originating in different ways may be obtained. In the first place, gas that was present in solution in the liquid metal and remains to some extent in solution in the solid metal will be obtained. In addition, some of this gas which was soluble in the liquid but not in the solid will be extracted from the cavities, and along with it gases that are practically insoluble in both liquid and solid, but are produced by a reaction during solidification, will be obtained. Finally, as the extraction of gases from metals usually means heating under reduced pressure, oxygen or nitrogen may be extracted from oxides and nitrides, and reactions leading to the formation of compound gases may be promoted. Thus, if copper containing copper oxide and oxygen in solid solution is heated *in vacuo*, the oxygen in solid solution is first removed. Then oxygen from the oxide goes into solution to restore the equilibrium and is in turn removed. In this way the oxide is eliminated and all the oxygen is extracted just as if it had been present as a gas. Again, when steel containing oxide and carbide is heated *in vacuo*, oxygen and carbon may react at the surface to form CO. More oxygen and carbon will then diffuse to the surface and form CO, while equilibrium is restored by further oxygen and carbon going into solution from the oxide and carbide. Thus CO may continue to be extracted from the metal as long as carbide and oxide remain. A similar phenomenon is exhibited by nickel containing carbide and oxide, and from aluminium methane may be obtained as a result of a surface reaction between hydrogen and carbon (from carbide). Thus, the gases extracted from metals by heating *in vacuo* are not necessarily present in solution or in cavities, but may be derived from adsorbed films, the direct decomposition of carbides, oxides, or nitrides, or from reactions between carbides and oxides, carbides and hydrogen, oxides and hydrogen, or nitrides and hydrogen.

The Solubility of Gases in Metals.

When molten iron is in contact with oxygen a reaction occurs at the metal-gas interface and oxide is formed. This oxide then dissolves in

the molten metal until it becomes saturated. Thereafter, further oxide formed remains on the surface of the metal and forms a slag which increases in thickness until all the metal is converted to oxide. Similar conditions arise when molten copper is in contact with oxygen, but different conditions result in the case of aluminium, for the oxide of this element is not appreciably soluble in the metal and therefore a surface layer of oxide is formed at an early stage of oxidation. In general, however, when the gas concerned forms a compound with the metal, it is the solubility of the compound and not of the gas that is considered. Thus iron is said to dissolve 1.1 per cent. of FeO at its melting-point and 2 per cent. at 1,700° C., while copper is said to dissolve 4.3 per cent. of Cu_2O at its melting-point and 10 per cent. at 1,175° C. Similarly,

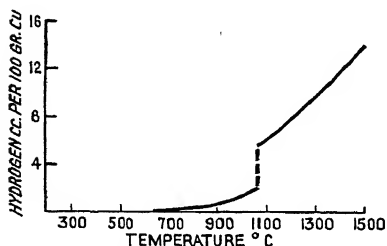


FIG. 223. Solubility of hydrogen in copper.

when iron dissolves nitrogen it is a nitride that goes into solution, and when iron or copper dissolves sulphur dioxide it is sulphides and oxides that go into solution. All these compounds are more soluble in the molten than in the solid metal, but they do not give rise directly to gas evolution, for the amount that is insoluble in the solid forms a distinct constituent, viz. oxide, sulphide, or nitride in the cast

metal. Thus no blowholes are formed in iron containing oxide, sulphide, or nitride, nor in copper containing oxide or sulphide unless the molten metal also contains some other substance that will react with these constituents to form gas, e.g. carbon in steel and hydrogen in copper, or unless two of the constituents can react together to form gas, as when SO_2 is formed from oxide and sulphide in copper.

True gas-metal solubility occurs when the gas remains as a gas when dissolved in the metal, and this phenomenon is most clearly displayed by hydrogen which does not form compounds with the common metals. It does, however, form compounds with certain metals, e.g. palladium and titanium, and is taken up by them under suitable conditions until the amount of gas dissolved approaches the ratios Pd_2H and TiH_2 . The solubility of hydrogen in the common metals increases with temperature, undergoes a marked increase at the melting-point, and then rises again with the temperature. A typical curve showing the solubility of hydrogen in copper is given in Fig. 223. A similar curve is obtained for nickel, and that for iron is also similar except that there is a marked increase in solubility at the $\alpha \rightarrow \gamma$ change in addition to that at the melting-point. In the case of aluminium the conditions differ in that there is no measurable solubility in the solid metal, although the fact that hydrogen can diffuse through aluminium indicates that the solubility is not zero.

It will be seen from Fig. 223 that solid copper at the melting-point

dissolves about 2 c.c. of hydrogen per 100 gm. of metal, while molten copper dissolves about 5.5 c.c. at the melting-point, and 14 c.c. at 1,500° C. This figure is based on the results of Sieverts and Röntgen and Moller. Bircumshaw (237) has determined the solubility of hydrogen in molten aluminium to be 0.23 c.c. per 100 gm. of metal at 700° C., 0.87 c.c. at 800° C., 1.87 c.c. at 900° C. and 3.86 c.c. at 1,000° C. The solubility in the solid metal was found to be practically zero, but Smithells and Ransley (238) have shown that hydrogen can diffuse through aluminium at temperatures above 400° C., and hence there must be some degree of solubility. For iron, as for other metals, varying values for the hydrogen solubility have been obtained, but it appears to be about 30 c.c. per 100 gm. at a temperature just above the melting-point, and 13 c.c. per 100 gm. just below the melting-point. The solubility in nickel is about 35 and 18 c.c. per 100 gm. at temperatures respectively just above and just below the melting-point. Consequently, the four metals may be placed in the order—nickel, iron, copper, and aluminium from greatest to least solubility in both the liquid and solid state. All the values given above refer to atmospheric pressure, but it has been shown that the solubilities of gases in metals are roughly proportional to the square root of the pressure, so that the solubility at any pressure $P = S\sqrt{P}$, where S is the solubility at atmospheric pressure.

Oxygen in silver behaves in the same way as hydrogen in this and other metals, and is usually considered as a case of true gas solubility. Under atmospheric pressure silver dissolves twenty times its own volume of oxygen at temperatures just above its melting-point and this is liberated as gas when the metal solidifies. Allen (239) has shown, however, that when sufficient pressure is applied the evolution of oxygen is prevented and silver oxide appears in the solid metal as a eutectic with silver. Apart from the exceptional behaviour of silver it may be said that oxygen forms oxides with most metals, and that if these oxides are soluble in the molten metal they occur as constituents in the solid. Nitrogen forms nitrides with iron and chromium and these are soluble to a slight extent in iron and to a pronounced extent in chromium and iron-chromium alloys. It is, however, not taken up in appreciable amounts by other metals. Hydrogen is soluble as a gas in most metals and the solubility in the liquid is much greater than in the solid. Carbon monoxide and carbon dioxide are not soluble in liquid or solid metals and neither are water vapour or sulphur dioxide. These gases may, however, react with metals forming oxides, sulphides, carbides, and hydrogen, all of which may dissolve in the metal. Hydrocarbons like methane are also dissociated at liquid or solid metal surfaces and carbon and hydrogen may go into solution.

The true solubility of a given gas in a given metal under particular conditions of temperature and pressure is the amount of gas that enters into or remains in the metal crystals when equilibrium is established between the metal and the gas. If the pressure is reduced, some gas

comes out of solution in the metal; if it is increased, more gas goes into solution. Similarly, if the temperature is raised more gas is dissolved, and if it is lowered, some is liberated. Under equilibrium conditions, the solution and evolution of gas is therefore a reversible process controlled by temperature and pressure and the respective natures of the metal and gas. In practice, however, numerous factors have to be taken into account besides equilibrium conditions. In the first place, a certain time is required to reach equilibrium under any given conditions of temperature and pressure. If the surface of the metal is clean, this depends on the rate of diffusion of the gas in the metal, and it decreases very rapidly with fall of temperature, e.g. hydrogen diffuses through iron 100 times as fast at 800° C. as at 350° C. At temperatures considerably above the melting-points of the metals equilibrium is reached in comparatively short times, which vary, however, with the relations between the mass of the metal and the area of the gas-metal interface. If, after equilibrium has been established, the metal is slowly cooled, enough gas will diffuse out of solution to maintain equilibrium, but if cooling is not slow enough the metal will become supersaturated with gas. At solidification, owing to the marked change in solubility, a considerable amount of gas will be evolved, but unless this takes place very slowly the solid metal will contain more gas than is actually soluble. In cooling from the freezing-point, gas will continue to escape from the metal if sufficient time is allowed, but as the rate of diffusion decreases rapidly with temperature, metals will tend to become more and more supersaturated as the temperature falls. In practice, therefore, metals that dissolve sufficient amounts of gas when molten will be supersaturated with this gas at atmospheric temperature, and at this temperature, owing to the slow rate of diffusion, evolution of the gas will be slow (except in the case of nascent hydrogen). If the metal is exposed to a vacuum at atmospheric temperature a certain amount of gas will be extracted, but the rate of extraction will soon become negligible. On raising the temperature and thus increasing the rate of diffusion, the rate of extraction of the gas under the vacuum will increase, but in general equilibrium will not be reached until the metal is melted, unless very long times of heating are employed. It follows, therefore, that at low temperatures metals may continue to hold in solution considerable quantities of gas in excess of the equilibrium value, and they may remain in contact with a gas for a long time without dissolving the equilibrium amount.

Owing to the operation of the time factor, equilibrium conditions between gases and metals are difficult to establish in practice, and they are not generally attained except in laboratory experiments. Furthermore, a number of other factors intervene. Except during special degasifying treatments, metals are not exposed to vacua or simple gas atmospheres, and the mixed gas atmospheres to which they are usually exposed have complicated effects. Oxygen, e.g., produces a film of oxide on liquid and solid aluminium and this tends to prevent the

absorption of hydrogen from the atmosphere or the liberation of previously dissolved gas from the metal. When the oxide of the basis metal is soluble it does not have this effect until after the limit of solubility is reached, but insoluble oxides of other constituents are usually present, and form surface films which interfere with the passage of the gas. Thus, if the metal that is melted contains a large amount of gas to begin with, it may retain more than the equilibrium amount when it is cast. Alternatively, a metal may be melted in an atmosphere that permits a certain gas to be dissolved, but the realization of equilibrium between this gas and the metal may be prevented by surface layers of oxides or of slags produced by the addition of fluxes. In addition to the effect of surface layers the 'pick-up' of gas is affected by the composition of the molten metal. The presence of soluble oxide, for example, tends to prevent solution of hydrogen, for the oxide reacts with it to form water vapour which is not soluble.

The equilibrium conditions of gas solubility may therefore have little connexion with the amount dissolved by a molten metal, and they may not have much influence on the amount taken up by or extracted from a solid metal. It appears that nascent hydrogen may diffuse into solid metals and accumulate in cavities where it exists under pressure as molecular hydrogen or water vapour. Thus, metals that contain cavities may take up more of this gas than is actually soluble, and as nascent hydrogen may be produced by adsorption at the metal surface, this can occur even when the metal is in contact with molecular hydrogen. The amount and composition of the gas extracted from a solid metal will, in general, have little to do with equilibrium solubility, for it will consist largely of gas extracted from cavities or even produced by chemical reaction during the process of extraction.

Factors affecting the Evolution of Gas and the Trapping of Gas Bubbles.

The first of the factors that has to be considered is the origin of the gas and of constituents that react to form gas. In so far as gas which exists in solution as such and is liberated at solidification by a change in solubility is concerned, it will be evident from what has already been said that attention may be confined to hydrogen. Oxygen dissolves as oxide, nitrogen as nitride or not at all, sulphur dioxide as sulphide and oxide, water vapour as hydrogen and oxide, while carbon monoxide and carbon dioxide are not appreciably soluble. These are the principal gases with which metals come into contact and the only one that dissolves as a gas and is liberated by a change in solubility is hydrogen. The other gases which dissolve as compounds may give rise to the evolution of gas by reactions between these compounds (oxide and sulphide) or between a compound and hydrogen or carbon.

Hydrogen may be present in the metal before melting or it may be picked up directly from the furnace atmosphere or by the dissociation of water vapour. Electrolytically refined copper contains substantial

amounts of hydrogen and this is difficult to eliminate. Thus Allen (240) has shown that only a small proportion is given off when the solid metal is heated. Rapid evolution takes place on melting, but some hydrogen remains even when this is carried out under reduced pressure. For complete removal it is necessary to heat the metal for about 1 hour at $1,150^{\circ}\text{C}$. under a pressure of less than 60 mm. of mercury. In practice, the hydrogen is usually eliminated by oxidation, which promotes the formation of insoluble water vapour, but as this has to be followed by removal of the oxide, hydrogen is again picked up from the atmosphere. At this stage the conditions are substantially the same whether the copper has been electrolytically refined or purified by oxidation, and as will be shown later, the final stage in the satisfactory casting of copper is the correct adjustment of the oxygen-hydrogen ratio. The copper thus produced is known as 'tough pitch' and contains about 0.04 to 0.05 per cent. of oxygen which is enough to prevent substantial solution of hydrogen. Aluminium as melted may also contain hydrogen, and Hanson and Slater (241) have produced evidence that this is due to the absorption of nascent hydrogen formed by electrochemical corrosion in a moist atmosphere during storage. As hydrogen is practically insoluble in solid aluminium, the gas thus absorbed must accumulate in cavities. In discussing this subject Zeerleder suggested that the hydrogen present in aluminium that has been exposed to the atmosphere may be present in water combined in the corrosion product and dissolve in the metal when the water vapour is dissociated during melting. In any case, whether or not hydrogen is present in the metal as melted, it may be picked up by copper, aluminium and its alloys, and steel during melting, either by direct solution of hydrogen or by the decomposition of water vapour in the furnace atmosphere.

The other constituents involved in the liberation of gas, e.g. oxides, sulphides, and carbon may also be present in the metal as melted or taken up during melting, and in the latter case the pick-up may be an essential feature of the melting-process, as in the case of oxide in the manufacture of steel or the fire-refining of copper, or purely incidental, as in the pick-up of sulphide in these same processes. Whatever their origin, the gases that give rise to difficulties in the case of the three most important metals are hydrogen liberated from solution, water vapour formed by the combination of hydrogen and oxide, and carbon monoxide formed by the combination of carbon and oxide. In aluminium and its alloys the liberation of hydrogen is the principal factor, for there is no reaction between this and aluminium oxide. In copper and its alloys the liberation of water vapour is the usual cause of gas cavities, and in steel the most important factor is the evolution of carbon monoxide, but water vapour and hydrogen may also play a part.

If a metal is melted in a crucible and then cooled slowly, gas coming out of solution as a result of a change in solubility or a reaction in the metal may escape from the surface by diffusion so long as the surface

of the metal is not covered by a film that prevents this. If, however, the cooling is not sufficiently slow the gas will not escape rapidly enough, and the metal will become increasingly supersaturated as the temperature falls. If the formation of a solid crust on the exposed surface of the metal is prevented, solidification will begin at the walls of the crucible and proceed upwards and inwards. As dissolved hydrogen, oxides, and carbon are less soluble in the solid than in the molten metal, the formation of solid will lead to an increase in the concentration of these in the liquid, and this will in turn increase the degree of supersaturation with respect to hydrogen and accelerate the reaction between it and oxide or between carbon and oxide. Unless the rate of solidification is very slow the gases thus concentrated in the liquid will not escape at the requisite rate by diffusion.

Under conditions of very slow cooling followed by slow freezing proceeding from the bottom and sides of the crucible towards the top, it is possible for a certain amount of gas to escape by diffusion. But if the rate of cooling is faster or the amount of gas dissolved or generated is greater, this condition will not be realized and gas bubbles will form. For this to occur, the internal pressure of the dissolved gas must overcome the resistance of the hydrostatic pressure and surface tension of the metal. The resistance of the surface tension is greatest at the very beginning of bubble formation, i.e. when the diameter of the bubble is very small. It is therefore the most important factor in tending to prevent the first formation of bubbles, and it is doubtful whether these could form in molten metals in the absence of nuclei in the form of inclusions or solid crystals. But once a small bubble is formed, the resistance of the surface tension diminishes as it grows, and as the hydrostatic pressure remains constant, the bubble may readily increase in size until equilibrium is established between the pressure of the gas in the bubble and its internal pressure in the metal. From the point of view of bubble formation, some solubility of the 'insoluble' gases, water-vapour, and carbon monoxide must be supposed. This is also necessary in order that the reactions which lead to their formation may take place. The reaction between hydrogen and cuprous oxide must, for example, result in the first place in the production of a certain amount of water vapour that remains in solution, and supersaturation of the liquid with respect to this will have the same effect on bubble formation as supersaturation with respect to hydrogen.

Gas bubbles do not begin to form until the internal gas pressure reaches a certain magnitude, i.e. until the metal is highly supersaturated. This is influenced in the first place by the concentration of hydrogen, oxide, and carbon in the metal at the beginning of cooling. It is also influenced by the rate of cooling which controls to some extent the amount of gas that escapes by diffusion, and finally it is influenced by the process of freezing, for as this proceeds, the concentration of hydrogen, oxide, and carbon in the residual liquid increases. These

factors, by controlling the internal pressure of the gas, determine whether bubble formation will take place or not and at what stage in cooling or solidification it will begin. Once bubbles have formed they increase in size readily by the diffusion into them of gas from the surrounding metal, and equilibrium may soon be reached between the pressure of gas in the bubbles and its internal pressure in the surrounding metal.

In general, metals do not cool and solidify quietly in the vessels in which they were melted, but are poured into a cold or comparatively cold mould. Freezing begins immediately at the metal-mould interface and proceeds towards the interior. Meanwhile, more metal is being run in and creating turbulent conditions. This turbulence tends to promote the evolution of gas in bubble form at an earlier stage than that at which it would occur under quiet conditions. It must therefore be taken into account in considering the evolution of gas in this form.

In practice, metals do not contain sufficient gas or compounds that generate gas to give rise to the rapid evolution of this from the metal before it is poured into the mould. Consequently, when considering the evolution of gas we have to deal with conditions under which solidification and gas evolution are proceeding at the same time. It is because of this that the problem of blowholes when considered as a whole is very complicated. In the first place, the evolution of gas in bubble form may be promoted by the increase in internal gas pressure resulting from the drop in temperature that occurs in the mould, supplemented by the effect of agitation. In this case gas evolution will begin as soon as the metal enters the mould. If the gas content is not sufficient to do this, no bubbles will form until the gas and the reacting compounds are concentrated in the liquid by the formation of solid. Under these conditions bubbles may begin to form at any stage between the beginning and end of solidification. In addition to the beginning of gas evolution its continuance must also be considered. If bubble formation does not begin until near the end of solidification it will soon come to a stop by the completion of solidification, but if it begins at an early stage it may either proceed almost to completion while the bulk of the metal is liquid and thus most of the gas will escape, or it may continue at a steady rate as long as liquid metal remains. In this connexion there appears to be a marked difference between the evolution of hydrogen and that of gases formed by reactions. In the case of hydrogen the formation of bubbles begins when the internal pressure of the gas is sufficient to overcome the surface tension and hydrostatic pressure of the metal. Once bubbles are formed, however, hydrogen may continue to diffuse into them until the pressure of gas in the bubbles equals the internal pressure in the metal. If, in the first instance, the metal was highly supersaturated with hydrogen, this should result in the rapid formation of large bubbles, and the internal gas pressure should soon decrease to a value below that required to form bubbles. The evolution of hydrogen, if it begins when the bulk of the metal is molten, should thus be a

fairly rapid and sudden process. In the case of gases formed by reaction, however, the conditions are different. Before bubble formation begins, the reaction between, say, carbon and iron oxide will have proceeded until the metal is supersaturated with carbon-monoxide. When the internal pressure of this reaches a certain value, bubbles will begin to form, and the degree of saturation of the metal will tend to decrease. This, however, will tend to promote the formation of more carbon-monoxide and thus to maintain the gas-pressure constant. In general, therefore, the evolution in bubble form of a gas produced by a reaction will be likely to continue for a considerable time, but whether the rate increases, decreases, or remains constant, and the total length of time for which it continues will be influenced by the balance between the reduction of the carbon and oxide content by gas formation, and the increase in the concentration of these by the formation of solid.

In considering gas evolution and its effect on blowholes, the beginning and continuation of bubble formation must be dealt with in relation to the progress of solidification, for it is through bubbles becoming entangled in or surrounded by crystals that blowholes arise. Bubbles formed at an early stage in solidification may escape from the metal and this is particularly so in the case of ingots cast in moulds with an open top. The extent to which they escape, however, depends on the position in which they are formed with respect to the solidifying metal. If they are formed near the liquid-solid interface because of the concentration of gas produced there by the advancing solid, they may be entrapped between the growing crystals. If, however, they are formed in the middle of the ingot by the drop in temperature and turbulence they have more chance of escaping. The later the stage in solidification at which bubbles are formed, the less opportunity do they have of escaping from the metal (or rising to accumulate under the crust), and the limiting case is reached when gas bubbles are formed just before the last traces of liquid solidify. In this case the gas cavities are situated between the crystals and between the branches of the skeletons, and instead of being spherical or elliptical in shape they tend to take the form of the interstices in which they are located. As the number of bubbles entrapped and the positions in which they are entrapped depend on the process of solidification as much as on the conditions that lead to the evolution of gas, further discussion of this may be postponed until solidification has been considered.

Prevention of Gas Unsoundness.

The methods of preventing and controlling the unsoundness that results from the entrapping of gas liberated in bubble form may be classified according to whether they (1) remove gas already present and prevent further absorption, (2) remove and prevent the formation of constituents that react to form gas, or (3) cause solidification to take place in such a way that gas is not evolved, or if evolved, is able to escape.

Existing gas may be removed and further absorption prevented by melting metals *in vacuo* or in an inert atmosphere. If, for example, electrolytic copper containing hydrogen is melted *in vacuo*, the hydrogen will diffuse out of the metal, and if the time is long enough and the temperature high enough all the gas will be extracted. No more will be picked up so long as the vacuum is maintained. This method is extensively used in laboratories, but has not yet been applied to any great extent in industry. In the past, great difficulties were encountered in constructing and operating vacuum furnaces, but the introduction of the high-frequency induction furnace has greatly facilitated the industrial use of the vacuum, and this type of melting is being employed to some extent. Melting in an inert atmosphere has a very similar effect, for the dissolved gas diffuses into the atmosphere until its internal pressure in the metal balances its partial pressure in the atmosphere. As the latter may be made zero, or at any rate very small, the former may also be reduced to negligible proportions if sufficient time is allowed. Allen (240) has shown that sound castings may be obtained when small amounts of electrolytic copper are kept molten for about 30 minutes in nitrogen, carbon monoxide, or carbon dioxide, and in a recently developed process for making copper free from hydrogen, oxygen, or deoxidizers an inert atmosphere is used to prevent the pick-up of oxygen or hydrogen during casting (Chapter XV).

Vacuums and inert atmospheres are difficult to maintain under industrial conditions and, as all the gas must be withdrawn at the metal surface, the time required for diffusion is considerable, and may be greatly increased if any kind of film exists on the surface of the metal. In view of this, a simpler and more rapid method has been developed. This consists of bubbling an inert gas through the molten metal just before casting. Each bubble of inert gas rising through the molten metal acts like a small inert atmosphere produced within the metal. Hydrogen diffuses into the bubbles until its partial pressure there balances its internal pressure in the metal. Each bubble therefore carries away a certain amount of gas and if the operation is continued long enough most of it can be removed except in so far as more may be picked up from the atmosphere. This method was first used by Archbutt (242) who succeeded in removing hydrogen from aluminium alloys by treating them with nitrogen. About the same time Prytherch (243) found that hydrogen could also be removed from copper by bubbling nitrogen through the molten metal for 15 to 20 minutes. The best results are only obtained when the nitrogen is dry, for otherwise the metal is contaminated with hydrogen produced from the decomposition of the water vapour. Many developments have followed since the first discovery of the efficiency of gas treatment. It has been shown that copper may also be degasified by treatment with carbon monoxide, and that the treatment of aluminium and its alloys with chlorine, boron trichloride (244), titanium tetrachloride (245) or with mixtures of these

gases and nitrogen is more effective than simple nitrogen treatment. When aluminium is degasified with nitrogen or chlorine, the crystal structure is coarse, but when the treatment is carried out with boron trichloride or titanium tetrachloride, a fine grained structure which persists after remelting is obtained. The process resembles the removal of gas by melting in an inert atmosphere, but it is far more effective, because the gas does not have to diffuse to the surface to escape, but is picked up in the interior of the melt. Chlorine, boron trichloride, and titanium tetrachloride are not inert to aluminium and its alloys, and the advantages possessed by them from the point of view of degasification seem to depend on their chemical action. When molten aluminium is oxidized, an oxide skin that is very resistant to the passage of gas is formed, and Rosenhain (246) has suggested that when nitrogen is passed through aluminium, small traces of moisture or oxygen in the gas may result in the formation of oxide skins on the gas bubbles. This would prevent the diffusion of hydrogen into them. When the nitrogen is mixed with chlorine or chlorides, the latter appear to dissolve or flux the films round the bubbles, and thus the diffusion of hydrogen from the metal to the bubbles is facilitated. The action of titanium tetrachloride in refining the grain-size of aluminium alloys is quite distinct from its degasifying effect, and may be produced by adding metallic titanium.

The different methods of degasifying aluminium have been investigated by Hanson and Slater (241) who found that the results varied with the composition of the alloys, the temperature at which the treatment was performed, and the scale on which the work was carried out. Laboratory experiments with 3-lb. melts showed that an improvement in soundness could be obtained by treatment with either nitrogen or chlorine, but the best results were obtained by using a mixture of the two gases in equal proportions. Treatment with this mixture at a temperature of 700° C. for 10 minutes effectively removed all unsoundness from 3-lb. melts, and experiments with 60-lb. melts in an oil-fired furnace gave results in close agreement with those obtained in the laboratory. With 300-lb. melts in a gas-fired furnace fairly satisfactory results were obtained when the temperature did not exceed 700° C., but when it reached 760° C. the results were much less satisfactory. It appeared that at this temperature the rate of absorption of gas from the furnace atmosphere was more rapid than the rate of elimination of gas by the nitrogen-chlorine treatment. Treatment with titanium tetrachloride was found to refine the grain-size of all the alloys used, but although perfectly sound castings of certain alloys were thus obtained other alloys remained moderately unsound.

The rapid evolution of carbon monoxide which accompanies the removal of carbon during the manufacture of steel tends to eliminate hydrogen in much the same way as does the treatment of copper or aluminium alloys with certain gases. As a result of the reaction between oxygen and the carbon contained in the bath of metal, bubbles

of carbon monoxide are formed. As they rise through the melt the hydrogen dissolved in the steel tends to diffuse into them so that each bubble carries away a minute quantity of hydrogen. The rapid evolution of carbon monoxide from molten steel is known as the 'boil', and in the open-hearth process its duration and intensity may be controlled by varying the additions of iron ore and pig-iron to the bath. By prolonging the boil it should be possible to eliminate most of the hydrogen previously dissolved in the steel, but the exact effect of this cannot be estimated in the absence of information with regard to the rate at which hydrogen is absorbed from the furnace atmosphere during and after the boiling period.

Unsoundness due to the liberation of gas rarely occurs in brass, and Bailey (249) has shown that hydrogen or sulphur dioxide may be passed through molten 70/30 brass without producing gas unsoundness in the resulting casting. This is attributed to the high vapour pressure of the zinc which appears to prevent gas absorption. In confirmation of this, Hanson and Slater found that when an aluminium alloy containing zinc was heated to 950° C. and stirred vigorously so that volatilization of zinc occurred, a sound casting was obtained. Phosphorus and arsenic when added to copper seem to act to a certain extent in the same way, for Allen (240) found that when 0.5 per cent. of phosphorus or 0.6 per cent. of arsenic was added to cathode copper, the formation of the blowholes associated with the presence of hydrogen was effectively prevented. Although they appear to eliminate hydrogen from cathode copper, these elements do not prevent the absorption of the gas when it is passed over the molten metal.

The usual method of eliminating hydrogen from electrolytic copper, and of preventing hydrogen uptake during the melting of this and other varieties of copper, is to oxidize the molten metal and thus promote the formation of insoluble water vapour. To do this, the oxidation must be carried to excess and the surplus oxygen later removed. In the manufacture of steel, oxidation is necessary to eliminate carbon, &c., and it also eliminates hydrogen as water vapour. Again, however, oxidation must be followed by deoxidation, and the metal may then pick up hydrogen again. Similar methods are not applicable to aluminium and its alloys, for the oxide formed is not appreciably soluble and does not react with hydrogen to form water vapour. Consequently, with this metal, some other treatment such as the gas treatments mentioned above is necessary.

When unsoundness is due to a reaction involving soluble oxide and hydrogen or carbon, the formation of gas may be prevented by converting this oxide into a compound that does not react. This is the method used in obtaining sound steel and it is also used in the manufacture of phosphorized or deoxidized copper. In the case of steel, manganese, silicon, and aluminium are added, and these reduce the iron oxide and form oxides that do not react with carbon. Being insoluble

in the steel, these tend to rise out of it, and the extent to which this is permitted to take place determines the amount of oxide and silicate inclusions retained by the steel. The complete deoxidation of steel is known as 'killing', but for certain varieties this is not resorted to and a considerable amount of iron oxide is allowed to remain. Blowholes are formed when this steel solidifies, and in casting steel of this type the skill of the metallurgist is directed to controlling their position. Similarly, the formation of blowholes in copper may be prevented by adding phosphorus, calcium, lithium, arsenic, &c., but owing to the fact that the presence of residual amounts of the deoxidizers lowers the conductivity of the copper, the method is only employed for special varieties.

The foregoing methods of preventing gas unsoundness are designed to eliminate gas and compounds that react to form it. Other methods are available, however, for controlling solidification so that gas can escape, or for preventing the formation of blowholes by pressure. Archbutt (242) found that the major portion of the gas dissolved in aluminium could be eliminated if the metal was allowed to solidify slowly in the crucible in which it was melted, the top of the metal being stirred to prevent the formation of a crust. If, after solidification, the metal is rapidly remelted and cast, comparatively sound metal is obtained. This 'pre-solidification' treatment may also be applied successfully to copper, but it has not found much industrial application. Another method of avoiding gas unsoundness is to cause the casting to solidify from the bottom upwards. This method is suitable for ingots of simple shape, but it cannot be applied so easily to sand castings or permanent mould castings of varied shape. As long as the solid advances gradually from the bottom towards the top, the evolved gas will escape freely and no large blowholes will be formed. Gas liberated between the growing crystals or in the interstices of the dendrites may, however, give rise to the small type of gas cavities known as pinholes.

Parsons and Duncan (247) have devised a method of casting large steel ingots in such a way that solidification takes place from the bottom. Steel ingots are usually cast in vertical iron moulds, and solid advances from the sides towards the centre just as rapidly as from the bottom upwards. In the Parsons and Duncan process the horizontal dimensions of the mould are greater than the vertical. Its bottom consists of a heavy block of steel or cast iron which rapidly abstracts heat from the metal poured in. The sides of the mould consist of refractory brickwork and are heated to a very high temperature before the steel is poured. A firebrick cover, provided with holes for the escape of gases and for the insertion of gas or oil burners which supply heat to the top of the metal, is placed over the mould. When steel is cast in this mould, solidification begins at the bottom and proceeds towards the top, and consequently the gases liberated at solidification are not entrapped in the metal. The 'R.W.R.' process, which is being applied to the casting of aluminium and its alloys, is somewhat similar. The

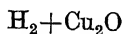
metal is poured into a mould preheated to the melting-temperature of aluminium in order to prevent solidification during pouring. When the mould is full, a copper plate is placed over the top and the mould is inverted. Water is then sprayed on the underside of the copper plate and the rapid extraction of heat from the bottom causes solidification to proceed from the bottom to the top and liberated gas is thus permitted to escape.

The formation of blowholes can also be prevented by casting under pressure. Thus Hanson and Slater (248) have shown that if gassy aluminium-alloy melts are cast in sand moulds under an external pressure of air or nitrogen, the pinholes are reduced in size and ingots of high density are obtained. With most aluminium alloys a pressure of 50 lb. per sq. in. is sufficient to remove all visible pinholes from a small 2 in. \times 2 in. ingot. The effect of the pressure is to prevent the growth of gas bubbles and, as a result of this, the cavities are much smaller and probably contain gas under pressure.

A further method of preventing gas unsoundness is by rapid cooling in the mould, i.e. by chill casting. This may appear to be in direct contradiction to the results obtained by the presolidification treatment, but it must be noted that whereas presolidification is a method of eliminating gas, chill casting, like casting under pressure, is a method of preventing the development of bubbles. Owing to the rapidity of solidification gas bubbles do not have an opportunity to form or grow, and consequently, although the gas is still present in the metal, it is retained in enforced solution in the solid or under high pressure in small cavities instead of under low pressure in large cavities. Chill castings are denser than sand castings but they frequently contain more gas.

Examples of Gas Unsoundness.

It may be produced in copper by the liberation of hydrogen or sulphur dioxide in the reaction between copper and water, or by the formation of water vapour in the reaction between copper and copper oxide. Of these causes of unsoundness, the most important. The final operation in the manufacture of copper is melting under oxidizing conditions to eliminate hydrogen from electrolytically refined copper and various other impurities from copper not previously refined in this way. The elimination of hydrogen depends on the reaction



decreased, the
in the furnace
by the metal.

224 due to Allen (240) shows how the hydrogen content of molten

copper decreases as the oxygen content increases, and it is clear that if the copper is oxidized to the extent of 0.15 per cent., little hydrogen will remain. Such an amount of oxygen is, however, undesirable in copper and after hydrogen and other impurities have been removed by oxidation, it is necessary to decrease it. This is done by 'poling', i.e. burning logs in the molten copper. At this stage the conditions are the same whether the metal was previously refined electrolytically or not. As the oxygen content diminishes, the hydrogen content increases. More hydrogen becomes available for combining with oxide to form water vapour during solidification, and the resulting cast metal tends to become increasingly unsound. It will be observed, however, in Fig. 224, that the hydrogen content does not increase rapidly until the oxygen content falls below 0.05 per cent., and, for this reason, the object aimed at in poling copper is to decrease the oxygen content to about 0.04 to 0.05 per cent. If it is higher than this, there is too much copper oxide in the cast metal; if it is lower, there is too much hydrogen to combine with oxide and the cast metal is very unsound. If, however, the oxygen content is adjusted to about 0.04 to 0.05 per cent. a satisfactory compromise between oxide content and unsoundness is effected.

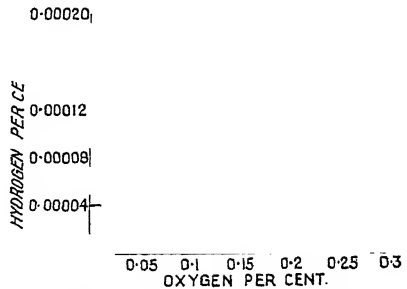


FIG. 224. Relations between O_2 and H_2 contents of copper.

When the molten metal is highly oxidized, the hydrogen content is too low to give rise to the liberation of appreciable amounts of gas during solidification. Ingots cast from such metal are sound, they have a depression on the top resulting from the contraction that accompanies solidification, and they contain substantial amounts of copper oxide. Such copper is said to be 'underpoled'. When the oxygen content of the molten metal is reduced below 0.04 per cent. by poling, the hydrogen content is high, there is plenty of this gas to react with copper oxide during solidification, and the resulting ingots are unsound. Owing to the amount of gas entrapped, such ingots show a bulge on the surface and the copper is said to be 'overpoled'. If, however, the oxygen content is adjusted to about 0.04 to 0.05 per cent., the resulting ingots are not sufficiently unsound to show a bulge nor sufficiently sound to show a depression. They consequently solidify with a flat top and this is known as 'tough pitch' copper. Besides decreasing the degree of unsoundness, the small amount of oxygen in tough pitch copper serves to improve the mechanical and electrical properties of the metal, for some of the detrimental impurities then occur as oxide and have less effect than when they are present as elements.

The oxygen necessarily present in tough pitch copper has certain disadvantages, the most important of which is that when the metal is

subsequently exposed to an atmosphere containing hydrogen, e.g. during oxy-acetylene welding or annealing in a reducing atmosphere, this gas penetrates the metal and reacts with the oxide to form steam, which being unable to escape, builds up a pressure and weakens the cohesion at the crystal boundaries. For certain purposes, therefore, the oxygen present in the metal must be finally eliminated or converted into a form that does not react with hydrogen. To accomplish this, deoxidizers are added just before casting. The one most generally used is phosphorus, but zinc, silicon, aluminium, magnesium, beryllium, calcium, calcium-boride, and lithium have also been used. These combine with the oxygen and form oxides that tend to rise out of the molten metal and copper free from copper oxide can be produced.

It is difficult, however, to adjust the additions of deoxidizers so that small amounts of the added elements will not remain in solid solution in the copper, and as these decrease the electrical conductivity to a greater extent than oxide does, deoxidized copper has a lower conductivity than tough pitch. Recently, however, the difficulty of having to choose between the presence of oxide or deoxidizers has been overcome by the method used in making oxygen-free high-conductivity ('O.F.H.C.') copper. In this process electrolytically refined copper is oxidized and poled as usual, then further deoxidized by running through a bed of charcoal. Thereafter the metal runs to a casting vessel and into the moulds. During this process an inert atmosphere surrounds the metal, and sound ingots free from oxide are obtained. The density of pure copper is 8.9, and by the method just described ingots with a density of 8.85 to 8.9 can be obtained, whereas that of the tough pitch variety is only 8.5.

Unsoundness in aluminium and its alloys is due almost entirely to the liberation of hydrogen which is soluble in the molten metal to the extent of 0.23, 0.87, and 1.87 c.c. per 100 gm. at 700°, 800°, and 900°C. respectively, and virtually insoluble in the solid. When the molten metal is saturated with hydrogen, a certain amount is liberated in bubble form during the early stages of solidification and escapes, but the gas responsible for unsoundness is that given off when solidification is nearly complete. This gives rise to the formation of irregular cracks and voids in the interstices of the dendrites and these are known as pinholes. As no reaction involving oxide is concerned in the liberation of gas from aluminium and its alloys, unsoundness cannot be controlled by adjusting the oxygen content or by adding deoxidizers. To obtain sound castings, it is necessary to restrict the amount of hydrogen picked up by the molten metal by preventing access of water vapour or hydrogen and overheating of the melt. Once absorbed, the hydrogen can be eliminated by treatment with gases as described in the previous section, or alternatively the gas liberated during solidification may be permitted to escape by using special methods of casting such as the 'R.W.R.' process.

With the exception of certain varieties of cast-iron, all the metals contract on solidification. When gas bubbles are entrapped, however, the expansion due to this compensates for the liquid-solid contraction and makes it easier to obtain castings that are free from contraction cavities. In many cases, therefore, the complete prevention of gas liberation is not aimed at, and this is particularly so in the casting of certain types of steel ingots. The principal cause of gas liberation in steel is the reaction between carbon and iron oxide which results in the formation of carbon monoxide, and this can be controlled by varying the extent to which the oxygen present is converted into a non-reactive oxide by adding manganese, silicon, and aluminium. In the manufacture of steel castings, ingots of alloy steel, ingots of carbon steel containing more than 0.15 per cent. of carbon, and ingots of steel containing less than 0.15 per cent. of carbon, when the best mechanical properties are required it is usual to add sufficient manganese, silicon, and aluminium to deoxidize the iron completely. Some gas is liberated during solidification, but little is entrapped in the solid metal. A considerable amount of contraction takes place on freezing and the steel is known as 'killed' or 'piping' steel. In steel containing less than 0.15 per cent. of carbon, blowholes in the ingot tend to weld up during rolling, and in order to avoid the difficulties associated with contraction, several varieties of ingots are made in which deoxidation is intentionally limited so that gas will be liberated and to some extent entrapped in the solid metal as blowholes. Ingots of this kind should be used only for low carbon steel which will subsequently be rolled or otherwise hot-worked to such an extent as to close the blowholes, and the various types will be described later.

Two distinct sets of problems are involved in the manufacture of killed steel and blown steel respectively. In the case of the former, the object is to reduce the iron oxide while leaving a minimum residue of inclusions in the metal. In the case of the latter, the object is to control the liberation of gas. Certain advantages are obtained by permitting the formation of blowholes in low carbon steel that is to be rolled, for during this operation those that are not too near the surface are welded up. If, however, they are near the surface, they are liable to be exposed to the atmosphere when the ingot is rolled. Their surface is then oxidized, they do not weld up, and they give rise to defects on the surface of the metal. Thus the object in casting gassy ingots is to avoid the formation of blowholes in the outer skin of the ingot, i.e. within about $\frac{1}{4}$ in. of the surface.

The principal cause of the liberation of gas from steel is the reaction

$$\text{FeO} + \text{C} \rightleftharpoons \text{Fe} + \text{CO}.$$

At any given temperature there is a minimum concentration of carbon and iron oxide below which the reaction will not proceed in the left to right direction. If this concentration is exceeded, CO will be formed in sufficient quantities to give rise to the formation of bubbles in the

molten metal, and this will continue until the concentrations of carbon and iron oxide are reduced to the equilibrium value. The higher the original concentration of the reactants, the more gas will be evolved before equilibrium is reached; but in dealing with the casting of steel, equilibrium conditions are not important, and what matters is not the amount of gas that can be evolved before equilibrium is reached, but the rate at which it is evolved in relation to the rate of solidification.

Whichever kind of steel is being made, the concentrations of carbon and iron oxide are not sufficiently high to cause the rapid liberation of CO from the molten metal in the ladle. Evolution of gas in bubble form only takes place in the mould where it is promoted by the agitation that accompanies the filling of the mould, the concentration of the reactants in the liquid by the formation of solid, and the action of the solid crystals in providing nuclei on which gas bubbles can form. As the concentrations of carbon and iron oxide increase together, the tendency for the reaction to take place also increases, and consequently it begins at an earlier stage and proceeds more rapidly. The same result is obtained if the concentration of either of the reactants is increased while that of the other remains constant. As in most cases the steel is being made to a specified carbon content, it is the iron oxide concentration that can be adjusted to determine the stage at which the rapid evolution of gas begins.

Three distinct types of ingots may be distinguished in the first place, namely, killed, rimming, and box-hat. These ingots are cast in vertical cast iron moulds and ink prints of vertical sections through different types are shown in Fig. 225, from the Fifth Report of the Heterogeneity of Steel Ingots Committee. They are obtained by sectioning the ingot and coating the surface with printers' ink and then taking a paper impression. Sound metal appears black, and blowholes and contraction cavities white. The three ingots at the left-hand side (I, II, and II*a*) represent the three types under discussion. No. I is a killed ingot in which no gas bubbles have been entrapped and which has a large cavity at the top caused by contraction on solidification. No. II is a rimming ingot. In casting such an ingot, the amount of unreduced iron oxide is adjusted so that the evolution of gas does not begin until a certain amount of solidification has proceeded inwards from the mould walls and until after the mould has been filled. Gas evolution is related to solidification in such a way that the outside of the ingot is solid and a sufficient number of gas bubbles are entrapped in the interior to eliminate a pipe like that shown at the top of No. I. Ingots of the box-hat type, illustrated by No. II*a*, Fig. 225, are obtained when the iron-oxide content is too high. A certain amount of solid is formed before gas evolution begins, but this is taking place rapidly while the mould is filling, and as a result, sufficient metal cannot be poured in. As the rate of evolution of gas diminishes, the level of the liquid in the mould falls and the resulting ingot only partially fills the mould. The ink print II*c*

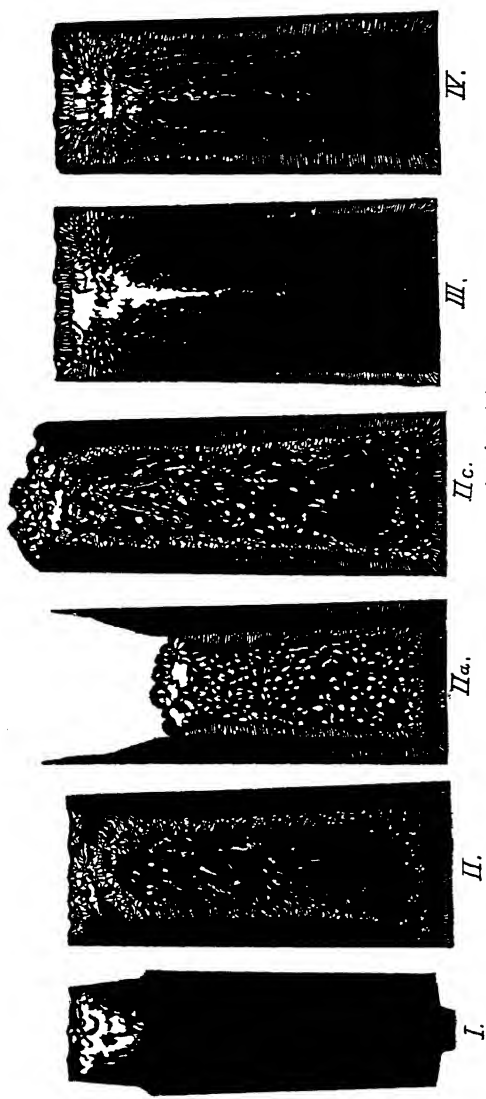


FIG. 225. Ink prints illustrating ingot types.
(Journal of the Iron and Steel Institute.)

represents an ingot of the 'rising' type which so far as gas evolution is concerned is intermediate between a rimming and a box-hat ingot. There is not sufficient evolution of gas while the mould is filling to diminish substantially the amount of metal poured in. Rapid gas evolution begins later and causes the liquid to rise in the mould. Solidification and gas evolution are so related that the amount of gas entrapped is sufficient to maintain the solid at the level reached by the liquid. Ink prints Nos. III and IV represent 'semi-killed' and 'balanced' ingots respectively. These types are intermediate between killed and rimming ingots in that they are not deoxidized to such an extent as to prevent the formation of blowholes nor permitted to gas to such an extent as to prevent the formation of pipe. As will be seen from the prints, the semi-killed resembles the killed, while the balanced resembles the rimming, in so far as the pipes and blowholes are concerned. Box-hat ingots are not made intentionally, but as there is a gradual transition from type to type throughout the series, killed (No. I), semi-killed (No. III), balanced (No. IV), rimming (No. II), rising (No. IIc), to box-hat (No. IIa), and as the amount by which the level of the liquid sinks in the box-hat may be much less than shown in the figure, there is sometimes not much difference between rising and box-hat ingots.

Although the evolution of carbon monoxide is the principal cause of blowholes in steel, the liberation of hydrogen and of water vapour formed by reaction between hydrogen and oxygen are also concerned. Certain amounts of hydrogen are contained in the pig-iron charged into the steel furnace and further quantities are introduced as water vapour in rust adhering to steel scrap, but the principal source of hydrogen is probably water vapour in the furnace atmosphere. When the elimination of carbon is taking place the bubbles of carbon monoxide rising through the molten metal have the same effect as passing an inert gas, and during this boiling period hydrogen tends to be eliminated. Not all of it is eliminated in this way, however, and in any case more may be picked up later, so that when the steel enters the mould it contains a certain amount of this gas. As hydrogen is more soluble in the liquid than in the solid metal, it will tend to be liberated at solidification and it will also tend to react with iron oxide to form insoluble water vapour. The evolution of hydrogen and water vapour must therefore supplement the effect of carbon monoxide in producing gas bubbles but the relations between these various gases are not yet understood. Although it is known that in the absence of other gas-forming constituents hydrogen alone, when present in sufficient quantities, will cause the formation of gas bubbles, and although it is known to be present in the gases evolved while steel is solidifying, its exact function in practice is not known, i.e. there is no evidence as to the amount of hydrogen actually contained in molten steel, nor as to whether such amounts as are present can initiate the formation of gas bubbles or simply increase the size of these by diffusing into them. In any case, most of the pheno-

mena associated with the evolution of gas from steel in practice appear to be capable of explanation without attributing any specific function to hydrogen except that it diffuses into the carbon-monoxide bubbles, and this gas liberation may be controlled by adjusting the additions of elements that react with iron oxide and do not appear to have any effect on hydrogen. Certain amounts of hydrogen are retained in solution in solid steel, particularly in ingots of the killed type in which there is no rapid evolution of carbon monoxide to carry it off. These small amounts (of the order of 0.0006 per cent.) are believed to be responsible for a type of defect known as 'flakes' which occur in large forgings particularly of alloy steels. These defects are known as flakes because of their appearance on a fractured surface passing through them, but they are actually minute cracks in the metal through which a fracture tends to pass. It appears that they are formed while the steel is cooling (below 300° C.) by pressure developed by the liberation of hydrogen from solution. (See also Chapter XII.)

SOLIDIFICATION OF CAST METALS

In considering solidification in Chapter V, attention was mainly confined to the way in which metal crystals grow. Assuming that crystallization began at nuclei distributed throughout the melt, the formation of crystal skeletons and the subsequent filling in of the interstices were described, and the effects of this method of crystal growth on the characteristic microstructure of cast metals was dealt with. This description sufficed as a basis for considering constitution and microstructure, but numerous other factors have to be taken into account in order to explain the general structure of a casting or ingot. In dealing with the constitution and microstructure of alloys, any small volume could be considered as being typical of the whole, but in dealing with castings and ingots, attention must be given to the general arrangement of crystals throughout the mass. This is known as the 'macrostructure'. It is built up when the metal solidifies, and it depends on the way in which freezing proceeds throughout the mass. When properly interpreted it provides a record of the conditions that prevailed during solidification, and by a study of it improvements in casting technique may be worked out.

The first factor that has to be taken into account in considering the solidification of cast metal is the temperature gradient which exists in all metals cooling from a higher to a lower temperature by the dissipation of heat from their surface, and in order to be able to neglect in the meantime certain complicating factors that arise when the metal is poured into a mould, the effect of the temperature gradient will be considered in relation to metals solidifying in the crucibles in which they have been melted.

Solidification of a Pure Metal in a Crucible.

The simplest conditions of solidification are realized when a pure metal is allowed to solidify in the crucible in which it has melted. The free

Solidification of a Solid Solution in a Crucible.

The solidification of solid solutions and such intermediate constituents as have a freezing range differs considerably from that of pure metals in that solidification takes place over a range of temperature, solid of progressively varying composition is produced, and the composition of the liquid changes gradually as solidification proceeds. These factors, combined with the characteristic manner in which metal crystals grow, introduce a number of complications into the solidification of solid solutions, and as will be shown in this and subsequent sections, there are numerous features of the process that are not yet fully understood.

In dealing with the solidification of solid solutions in Chapter V, it was supposed that crystals were growing from nuclei distributed throughout the melt and that consequently the conditions were the same whether we considered one crystal surrounded by liquid or the alloy as a whole. When we have to consider masses of solid solutions solidifying in crucibles and moulds, this assumption cannot, however, be maintained, and several factors in addition to those mentioned in Chapter V have to be taken into account. One of the most important of these is diffusion in the liquid. In Chapter V we dealt at length with the relations between selective freezing and diffusion in the solid, but we assumed that the solute rejected by the solid diffused so rapidly throughout the liquid that no variations in composition in the liquid need be supposed. This assumption is justified when dealing with solidification taking place from numerous evenly distributed nuclei, for in the small amount of liquid surrounding each crystal a uniform distribution of solute can soon be established by diffusion. When, however, solidification is proceeding from the outside towards the interior of a mass of metal contained in a crucible, the liquid is all the molten metal remaining, and, as some of it is some distance from the advancing solid, a uniform distribution of the solute rejected by the liquid is not obtained unless cooling is exceptionally slow. The effect of variations in the composition of the liquid must therefore be considered.

For the present purpose, no further discussion of the relations between selective freezing and solid diffusion is required, and it will suffice to repeat that under all ordinary practical conditions the individual crystals formed vary in composition and that this variation increases with the rate of their growth. Attention may be confined to the relations between rate of cooling and liquid diffusion, and to the effect of temperature gradients. If the rate of abstraction of heat is very slow, the conditions realized during the solidification of a solid solution are similar to those realized with similar cooling in a pure metal, except that crystals of varying composition are produced. The temperature gradient is not sufficiently steep to cause solidification to take place entirely by the advance of solid from the outside towards the interior. It takes place to some extent in this way, but new nuclei are constantly

appearing at points in advance of the solid, and in some cases considerably in advance, equiaxed crystals are thus produced and the conditions resemble to some extent those described in Chapter V. If, however, the rate of cooling is increased so as to produce a temperature gradient steep enough to cause solidification to take place progressively from the outside to the centre, then different conditions are realized. Two different cases may be distinguished (1) when the solute rejected by the solid diffuses throughout the melt so that a substantially uniform distribution of solute is maintained, and (2) when the solute does not diffuse sufficiently and becomes concentrated in front of the advancing solid. These two cases will now be described, but it must be pointed out that the descriptions relate to extreme examples and any intermediate conditions may be obtained.

For the purpose of the present description, the solidification of a solid solution of zinc in copper may be considered. In such an alloy the crystals first formed at the surface will be richer in copper than the melt, and as a result the zinc content of the remaining melt will be increased. This increase takes place to begin with at the liquid-solid interface, but under the conditions we are at present assuming, this zinc is supposed to have time to diffuse throughout the melt so as to keep it uniform. If we suppose that the solid advances inwards by the formation of successive shells, then it is evident that the second thin shell will contain more zinc than the first, and the zinc content of the liquid will be further increased. Thus, in general, each successive shell of solid will contain more zinc than that previously formed, and the liquid will become progressively higher in zinc as solidification proceeds towards the interior. While this is going on, there will be some diffusion of zinc in the solid and from the liquid to the solid, but this will not be sufficient to eliminate the effects of selective freezing, and when solidification is complete the zinc content of the alloy will increase progressively from the surface to the interior. In other words, under the assumed conditions, the method of freezing described in Chapter V in relation to individual crystals growing in a melt will apply to the contents of the crucible as a whole.

Under the conditions assumed above, the tendency will be for columnar crystals to grow from the surface and extend to the point in the interior where solidification is completed, i.e. the heat-centre or the last region to reach the solidus temperature of the alloy. Owing to the fact that the temperature gradient in the crucible tends to decrease as cooling proceeds, the conditions will generally change at some stage in the cooling from those described above to those characteristic of slower cooling. When this occurs the progressive advance of solid from surface to heat-centre will become less pronounced, columnar crystals will give place to equiaxed, and instead of selective freezing affecting the solid as a whole, it will influence the individual crystals.

If it is now supposed that the rate of cooling is insufficiently slow

to permit uniform diffusion of the zinc rejected by the solid, it is evident that the formation near the surface of solid rich in copper will raise the zinc content of the adjacent liquid but not of that which is more remote. As increase in the zinc content of the liquid lowers the temperature at which solid can form from it, this means that solid can be formed from the liquid more remote from the existing solid at a higher temperature than from the liquid adjacent to the existing solid. In other words, the fact that the zinc tends to concentrate in the liquid in contact with the existing solid serves to promote the appearance of new crystals away from the surface of this solid. The existence of a temperature gradient and the fact that solid is deposited on existing crystals more readily than new ones are formed, tends to prevent the formation of new crystals when the concentration of zinc in contact with existing ones is small. When, however, the rate of abstraction of heat is sufficiently rapid to produce a pronounced concentration of zinc in the liquid surrounding growing crystals, the advance of solid from the surface to the centre tends to take place by the formation of successive generations of new crystals, each of which is formed slightly nearer the interior than the surface of the previous generation. At the time of the first formation of a new generation, some liquid, rich in zinc, exists between it and the previous one, and this is later absorbed by the growth of both sets of crystals.

When solidification takes place in the manner just described, it does not proceed uniformly from the outside to the centre of the cooling metal and it does not result in the production of a solid that varies progressively in composition. Each new generation of crystals begins to form in liquid that is substantially of the same composition as the original melt, and the variations in composition resulting from selective freezing are confined to the individual crystals and the bands occupied by successive generations, and do not affect the mass of metal as a whole. Thus, although increasing the rate of cooling increases the heterogeneity of the individual crystals as described in Chapter V, it has the opposite effect when a crucible or mould full of metal is considered as a whole, i.e. it tends to produce greater homogeneity.

It should not be supposed that the successive generations of crystals mentioned above appear at regular intervals at a definite distance from a uniform solid shell, thus giving rise to a solid mass that consists of a series of layers corresponding to different generations of crystals. Actually the process will be quite irregular, so that, although solid advances from the outside to the inside by the appearance of successive generations, all the crystals that may be supposed to belong to one generation do not appear at the same time, nor do they lie on a smooth line parallel to the cooling surface. As already stated, the two cases described above are extremes, and various intermediate conditions may arise. Thus, although one rate of cooling may give rise to columnar crystals and an increase in the zinc content from the surface to the

centre, and a considerably faster rate of cooling may give rise to small equiaxed crystals, and a substantially uniform distribution of zinc, an intermediate rate of cooling may give rise to shorter columnar or equiaxed crystals formed in successive generations and fitting irregularly into each other. This should be accompanied by some variation in zinc content within the sphere of each generation and also from the surface to the centre of the mass.

The Effect of Skeleton Growth.

In the foregoing sections the solidification of pure metals and solid solutions in crucibles has been considered without regard to the characteristic manner in which metal crystals grow by the formation of primary skeletons and the subsequent filling in of the interstices. When this mode of crystal growth is taken into account, it is found to modify to a pronounced extent the mechanism of solidification of solid solutions and alloys consisting of primary constituents and eutectics, which resemble solid solutions from the point of view of solidification, except for the fact that the last stage occurs at constant temperature.

When the conditions are such that solidification takes place from isolated nuclei distributed throughout the melt, the behaviour of skeleton crystals is as described in Chapter V except for the fact that the feeding of the growing crystals by liquid was not considered there. When, however, solidification takes place progressively from the outside to the centre by the formation of columnar or successive generations of equiaxed crystals, then skeleton growth introduces important modifications into the mechanism of solidification described above. As the crystals grow in the first place by the formation of branched skeletons, solidification from the surface to the centre does not consist of the advance of an even wall. At any stage the farthest-advanced portion of the solid consists only of branched skeletons, and completely solid metal does not begin until some distance nearer the cooling surface. Consequently, the metal in the crucible may be divided into three zones: (1) the solid zone on the outside, (2) the pasty zone consisting of skeleton crystals in the liquid, and (3) the liquid zone. In a pure metal which solidifies at a constant temperature, the second zone is very narrow, and in any case, the effects of skeleton growth would be of little importance because of the absence of selective freezing. In solid solutions and alloys consisting of primary constituents and eutectics, the second zone is wider, and its width increases with increase in the temperature interval between the liquidus and solidus of the alloy concerned and with decrease in the temperature gradient. So many effects may arise from the relations between skeleton growth, selective freezing, advance of the solid from surface to centre and feeding of the growing crystals, that it is impossible to describe them all, and only some of the major aspects can be considered. For this purpose it appears best to consider a solid solution solidifying from the surface to the centre by the formation of columnar crystals.

When skeleton crystals are growing inwards from the surface of the crucible, the three zones already mentioned may be distinguished, i.e. the solid zone nearest the outside, the intermediate pasty zone in which the skeletons exist, and the inner liquid zone. In dealing with the solidification of a pure metal, it was stated that the advance of solid kept up with the freezing-point isotherm, and in dealing with the solidification of a solid solution, it may be said that the advance of the inner limit of the pasty zone keeps up with a moving isothermal line representing the liquidus temperature, while the advance of the inner limit of the solid zone keeps up with an isothermal line representing the solidus temperature. With a given temperature gradient, the actual width of the pasty zone must increase with the difference between the liquidus and solidus temperatures, and with a given range of solidification, the width of the pasty zone must increase with decrease in the temperature gradient.

The above reasoning is simple because it only takes account of skeleton growth and the fact that solidification takes place over a range of temperature. But difficulties arise when we introduce the effects of selective freezing, diffusion in the liquid, and feeding of the growing crystals. The skeleton crystals first formed near the surface are richer in copper than the melt, consequently the zinc content of the melt is increased, and the zinc thus rejected by the solid may diffuse to a varied extent throughout the remaining liquid according to the rate of cooling. The extent to which this takes place has a pronounced influence on what occurs in the pasty zone where solidification is in progress. In dealing with constitutional diagrams of alloys, as in Chapter V, what may be described as a closed system is assumed. What is going on in one part of the alloy is supposed to be the same as is going on in every other part, and the conditions at one point are not altered by what is going on elsewhere. The liquid being homogeneous and the temperature throughout being uniform, crystal nuclei are supposed to appear at points more or less equally distributed. From these, crystals begin to grow and owing to selective freezing the concentration of solute in the melt increases. Each crystal is supposed to grow at the same rate, so that after a certain amount of crystallization has taken place the relative proportions of solid and liquid in the alloy are the same whether we consider a small volume or the whole mass. From each growing crystal, solute is supposed to be rejected at the same rate, and the concentration of solute in the liquid is supposed to increase uniformly throughout the mass. In short, crystallization, selective freezing, and diffusion of solute are taking place at the same rate throughout the whole alloy, every part of the liquid is maintained at the same concentration and, in general, the conditions represented by the constitutional diagram may be held to apply to any particular crystal or the alloy as a whole.

The case is quite different when we consider solidification proceeding from the surface to the centre of a mass of metal. In this case we have not got a closed system. Solid is forming in one region while the metal

in another is still above its melting-point, and what takes place the solid point may modify the conditions at another.

Factors that promote Normal Segregation.

Assuming in the first place that cooling is slow and that the zinc rejected by the first skeletons diffuses to a considerable extent into the remaining liquid, then two points of difference between the present conditions and those supposed in Chapter V may be noted. In the first place, zinc diffuses away from the surface of growing crystals into regions where no crystallization is taking place, and thus the conditions in the vicinity of the growing crystals are altered. In the second place, the zinc that diffuses into regions in the liquid where no crystallization has occurred affects the process of solidification in these regions when it does take place. Thus, while the constitutional diagram assumes that at a given temperature there will be a particular proportion of solid and liquid, in the actual solidification of alloys there is a preponderating proportion of liquid because the temperature throughout the alloy is not uniform. This state of affairs persists until solidification is almost completed, and the existence of the liquid zone affects the conditions in the pasty zone, while selective freezing in the pasty zone alters the composition of the liquid zone.

Returning to the beginning of solidification on the walls of the crucible, it may be said that some of the zinc rejected by the first-formed skeletons diffuses away from the liquid from which the interstices of these skeletons will be filled. Thus the formation of a given amount of solid does not raise the zinc content of the liquid in its vicinity to the extent indicated by the constitutional diagram. Solidification begins in an alloy of a certain composition, but as it proceeds zinc is diffusing away into regions remote from this solid, and the conditions are the same as if the zinc content of the alloy were being gradually decreased. Thus, solidification will be completed at a higher temperature than the solidus of the original alloy, and the resulting solid will contain less zinc.

The zinc which diffuses away from the vicinity of the growing crystals raises the zinc content of parts of the melt where no solidification is taking place. The temperature at which solidification can begin in these is thus lowered, and the zinc content of the first-formed solid is increased. As the skeletons advance they therefore enter regions in the liquid where the zinc content has been raised by zinc rejected by previously formed solid, and this concentration of zinc in the residual melt becomes progressively greater as solidification proceeds. At each stage in their advance the skeletons begin to form from a liquid containing greater amounts of zinc, and consequently their zinc content increases.

What has been said about the subsequent filling-in of the interstices of the skeletons formed on the walls of the crucible applies to the skeletons formed nearer the interior. As the branches thicken some of

When rejected by the solid diffuses away into the liquid zone, so that the zinc content of the liquid in which the growth of any part of the skeleton is completed is lower than would be expected from the composition of the portion of the liquid in which the growth started. It is, however, higher than the zinc content of the liquid in which portions of the skeleton nearer the surface were completed.

Summarizing the above, it may be said that when the zinc rejected by the solid diffuses to a substantial extent throughout the liquid the conditions realized during the advance of the skeleton branches are similar to what would be obtained if zinc were being gradually added to the liquid, while the conditions realized during the subsequent thickening of these branches are the same as if zinc were being withdrawn from the liquid in their vicinity while they were growing. The skeletons formed on the walls of the crucible begin to grow from liquid of the same composition as the original melt, but as they advance they form from liquid of progressively increasing zinc content. The interstices of the skeletons formed on the walls of the crucible are filled with solid produced from liquid containing less zinc than would be supposed from the original composition of the alloy. As the distance from the surface increases, the zinc content of the interstitial metal increases; but so long as any liquid containing no solid remains, the zinc content of the interstitial metal is less than it would be in the absence of diffusion into the residual liquid. When only a small quantity of liquid remains, no zinc can diffuse away from the vicinity of the solid and the conditions then realized are as described in Chapter V; but the zinc content of the liquid is of course much higher than that of the alloy as melted.

It follows from the above that when the zinc rejected by the growing crystals diffuses to a substantial extent into the liquid, the average zinc content of the crystals increases from the outside to the interior of the solid alloy. The crystals near the surface have a lower average zinc content than the original metal, the zinc content increases with the distance from the surface, and towards the centre it becomes greater than that of the original melt. The fact that crystal growth takes place by the formation of skeletons and the subsequent filling of the interstices does not alter the conditions described in the previous section for similar amounts of diffusion. Thus, in addition to variations in composition within each crystal, there is a variation in composition from the surface to the centre of the alloy as a whole. Decreasing the rate of cooling decreases the first variation in composition by permitting solid diffusion, but it increases the second variation by permitting liquid diffusion.

The effect on the foregoing conditions of solidification of increasing the rate of cooling may now be considered. The more rapidly the metal is cooled the less does the zinc rejected by the solid diffuse throughout the remaining liquid, and consequently the smaller is the variation in composition from the outside to the centre of the completely solid alloy.

The limiting case is reached when all the zinc rejected by the solid forming at one point may be considered to remain in the liquid which will eventually solidify there. Thus, if the rate of solidification of the crystals formed at the surface of the crucible is so rapid that the zinc rejected by the first-formed skeletons remains in the liquid in their interstices until this also solidifies, then the average composition of the solid formed there will be the same as that of the original melt. Furthermore, so long as a sufficiently rapid rate of solidification is maintained, this condition will persist, i.e. if the rate of solidification is sufficiently rapid throughout the whole alloy the solid produced at each point will be of the same average composition as the melt, but if the rate of solidification falls below a certain value at a given distance from the surface then solid of progressively varying composition will begin to form. It follows from the above that, in so far as selective freezing and diffusion in the liquid are concerned, the limiting condition realized by increasing the rate of cooling is the production of a solid in which the average composition of the crystals is the same throughout. In practice, however, it is frequently found that cast metals display a variation in composition such that the concentration of the solute decreases from the surface to the centre. This is known as 'inverse segregation', while the previously described variation which results in the concentration of the solute increasing from the surface to the centre is known as 'normal segregation'. Neither of the types of segregation is more normal than the other, but that already described was the first to attract attention. It can be explained in terms of selective freezing and liquid diffusion, but to explain inverse segregation the feeding of the growing crystals must be taken into account.

Factors that promote Inverse Segregation.

In the pasty zone, where solidification is taking place, the metal consists of skeleton crystals with liquid in their interstices. As this crystallizes a contraction takes place and liquid from elsewhere tends to be drawn into the interstices. This is the process of feeding. As soon as solidification begins at a given point feeding of liquid towards this point also begins, and for completely solid metal to be produced this must continue until all the interstices of the skeletons are filled with solid metal. As the channels through which feeding must take place become increasingly narrower as the branches of the skeletons thicken, it is a process that occurs to a variable extent, but for the time being we are only concerned with the source and composition of the feeding liquid.

If we picture the pasty zone as containing skeletons in all stages of development, from minute fragile branches at the junction of this zone with the liquid zone to almost completely solid crystals at its junction with the solid zone, we may suppose that each part of it is fed with liquid from a point nearer the liquid zone. Thus the process of feeding

causes a general movement of liquid from the liquid to the pasty zone, and within this latter zone from its junction with the liquid zone to its junction with the solid zone. In other words the direction of movement of the feeding-liquid is the reverse of that in which solute tends to diffuse. Feeding eventually results in the formation of a cavity in the part of the cooling mass where the last residue of liquid would be expected to solidify, but for the present what we have to consider is how the liquid feeding into a given area affects the average composition of the solid formed there.

The average composition of the solid formed in a given region is the same as that of the liquid that solidifies in that region. Under the conditions assumed in Chapter V, the average composition of the solid formed in a given region is the same as that of the liquid that originally occupied that region. We have seen, however, that when substantial diffusion of the solute takes place while an alloy is solidifying from the surface towards the interior, the average composition of the solid formed in a given region is not the same as that of the liquid originally present there. As solute diffuses away while solidification is going on, the solid has a lower average content of solute than the liquid from which it began to form. It will now be shown that the liquid introduced into a given region as a result of feeding may tend to raise the average content of solute in the solid formed there.

It is convenient to consider the conditions realized during rapid cooling when all the zinc (or other solute) rejected by the growing crystals remains in their interstices. Under such conditions, and in the absence of feeding, the average composition of the solid in a given region will be the same as the composition of the liquid originally present there, i.e. the same as the composition of the original melt. At the inner limit of the pasty zone the contraction that accompanies the early stages in the growth of the crystals is compensated for by feeding from the liquid zone. The liquid thus introduced is (under the assumed conditions) of the same composition as the original melt, and also of the same composition as the liquid originally present in this region. Consequently, its introduction does not alter the composition of the solid. At a point in the pasty zone where solidification has proceeded further, the feeding liquid is supplied from another region in this zone where solidification is not so far advanced. The liquid supplied contains less zinc than that present at the same instant in the region being fed, because it has been concentrated to a less extent by the formation of solid. It contains more zinc, however, than the liquid originally present in the region under consideration, and therefore it increases the average zinc content of the liquid that solidifies there, and of the solid that finally occupies this region.

We see therefore that when the composition of the liquid in which no solidification has taken place is assumed to remain unaltered throughout the process of solidification, the beginning of skeleton formation in

each region takes place in liquid of the same composition as the original melt. As the skeleton in one region grows it is fed in the first place by liquid of the same composition as that in which it began to form, but as its growth proceeds it is fed by liquid coming from an adjacent region where solidification is now proceeding. As the zinc content in the region supplying the feeding-liquid is gradually increasing as a result of the progress of solidification, the effect of a regular supply of this liquid is to progressively increase the average content in the region being fed. Thus in general the process of feeding raises the average zinc content of the solid.

If we consider the crystals formed on the surface of the crucible, growing under the assumed conditions in the absence of feeding, we see that their average composition when completely solid is the same as that of the original melt. When they are progressively fed, however, by liquid of a higher zinc content than the original melt, then their average zinc content at the end of solidification will be higher than that of the original melt. Proceeding a step nearer the interior we find a similar process going on, but with one important difference, for while the crystals are being fed with liquid containing more zinc than the original melt, liquid containing still more zinc than this is being taken away to feed the crystals nearer the outer surface. It is evident from this that the crystals nearer the interior will contain less zinc than those nearer the surface, but the question arises how crystals other than those at the outer surface can contain more zinc than the original melt, in view of the fact that they would contain the same amount if the liquid in their interstices did not alter, and should therefore contain less if some of the liquid is drained away and replaced by liquid containing less zinc. It will be seen, however, that the liquid which feeds in has to replace that which drains away, and also to compensate for contraction in the region under consideration. The amount of the liquid that feeds in therefore exceeds that which drains away, and a greater amount of liquid containing less zinc may introduce more zinc than is lost in a smaller amount containing more zinc. Thus the average zinc content of the liquid that freezes in a given region may still be increased.

It has now been explained how the crystals formed on the outside may have a higher zinc content than the melt, and how those nearer the interior may contain less zinc than those at the surface and still contain more than the original melt. It remains to explain how the average zinc content of the crystals may decrease progressively towards the centre until a point is reached at which they have the same content as the original melt, and how it may continue to decrease beyond this and result in the formation of crystals containing less zinc than the melt. It is obvious that this must occur, for the melt contains a given amount of zinc, and if its concentration in the outer regions of the solid is raised, that in the inner regions must be lowered. Several factors may contribute to this, but only the two most important need be mentioned.

We have seen that in all regions except the outer shell, liquid is being drained away towards the outside and is being replaced by liquid from nearer the interior. We have seen also that the amount of liquid that feeds in must exceed that which drains away by an amount sufficient to compensate for contraction in the region under consideration. Although the liquid that drains away contains a higher proportion of zinc than that which feeds in, the zinc content of a given region may be increased because the amount of the latter liquid exceeds the amount of the former. This depends, however, on the quantitative relations between the amounts and compositions of the liquids concerned, and it is just as likely that the balance between draining and feeding will result in a decrease in the zinc content in a given region. When no liquid is draining away, feeding from the liquid zone (which is supposed to remain of the same composition throughout solidification) does not alter the composition of the solid. If, however, liquid that has been concentrated in zinc by the formation of solid in the pasty zone drains away from a given region and is replaced from the liquid zone, then the concentration of zinc in the resulting solid will be less than in the original melt. In order to explain the progressive diminution in zinc from the first to the last regions to solidify, it is therefore only necessary to suppose that as solidification proceeds increasing amounts of metal from the liquid zone are used in feeding. That this will be so follows from the statement already made that the amount of liquid which feeds in to a given region must exceed that which drains away. Thus considering solidification to proceed inwards by the formation of a series of shells, it is evident that the amount of liquid required to feed the first shell is simply the amount required to compensate for contraction in that shell. The amount required to feed the second shell is, however, the amount required to compensate for contraction in this shell plus the amount that was drained away to feed the first shell. Similarly, the amount required to feed the third shell is the amount required to compensate for contraction plus the amount fed to the second shell. Thus as solidification proceeds, increasing amounts of liquid are taken from the liquid zone to replace liquid of higher zinc content drained away towards the surface. In other words, the feeding liquid becomes lower and lower in zinc as solidification proceeds from the surface to the centre. Consequently, the zinc content of the resulting solid also decreases as the centre is approached.

In the very last region to solidify liquid is drained away and is not replaced, so that the zinc content in this region will be a minimum, and the portions of the crystals which should have the highest zinc content will be replaced by contraction cavities. A similar result may arise from inadequate feeding in other regions, and this is the second factor that contributes to a diminution of zinc content from surface to centre. Iokibé (250) and Allen and his collaborator (251) have studied the distribution of porosity and segregation in ingots and concluded that

inverse segregation is due to feeding. It is from these conclusions that the foregoing explanation has been worked out. These investigators also found that as the concentration of the solute decreased towards the interior of the ingots the density also decreased. This was shown to be due to the formation of contraction and gas cavities in the interstices of the skeleton crystals, and the decrease in solute in the interior regions may be partly attributed to this. The explanation is as follows: As the solidification of the metal proceeds the contraction cavities become larger and more frequent as a result of a progressive diminution in the extent to which adequate feeding occurs. This means that in the interior regions of the ingot liquid is drained away from the growing crystals and is not replaced, and as the liquid that has drained away is concentrated in zinc by the previous formation of solid the zinc content in these regions is decreased. The same applies to gas cavities formed in the interstices of the skeletons, for liberation of gas in these regions causes the ejection of zinc-rich liquid and prevents further feeding, and consequently the zinc content of the solid is decreased. According to this view, therefore, the size and number of inter-dendritic cavities increase as solidification proceeds, and as these occupy the places where the parts of the crystals most rich in zinc should solidify, their formation results in a progressive decrease in the zinc content from the regions that solidify first to those that solidify last. There is not a great difference between this process and that previously described, for the increase in contraction cavities with the progress of solidification is due to the increasing amounts of feeding required, neither is there a great difference between contraction cavities and inter-dendritic gas cavities, for as Allen has pointed out, the liberation of gas is frequently initiated by the contraction that accompanies crystallization.

Summary of Segregation.

It will be shown in subsequent sections that the exact distribution of the constituents of alloys throughout solid ingots is affected by several other factors besides those mentioned, but it may be said that the phenomena described in this section are the basic causes of segregation. Solidification proceeds from the surface to the interior by the advance of crystal skeletons and the subsequent filling-in of their interstices. Solute rejected by the skeletons tends to diffuse throughout all the liquid, and this in turn tends to produce an ingot in which the concentration of the solute increases from the first to the last region to solidify. At the same time, however, the process of feeding results in a constant flow of liquid from the centre towards the surface. The crystals at the surface are fed with liquid containing considerably more solute than that from which they began to grow, and consequently their concentration is increased above that of the melt. Subsequent layers of solid are produced under conditions which require the draining-away of liquid towards the surface and its replacement by liquid from nearer

the interior. As the pasty zone advances, the amount of liquid that drains away and has to be replaced increases, and as the feeding-liquid becomes progressively poorer in solute the concentration of this in the solid tends to diminish. Thus ingots in which the concentration of solute decreases from the surface to the interior tend to be produced. The distribution of solute in a solid ingot thus depends on the relations between the rate of skeleton growth, the rate of liquid diffusion, and feeding; and according to how these various processes balance an actual ingot may show either normal segregation or inverse segregation, or neither of these. When cast under similar conditions one alloy may show a greater tendency to either normal or inverse segregation than another, and when the same alloy is cast under different conditions some may produce normal and others inverse segregation. It would be difficult to reason out the exact effect on segregation of variation in the rate of cooling, but as slower cooling permits more diffusion in the liquid it may be expected to favour normal segregation. This is borne out by practice, and large or slowly cooled masses of metal tend to show normal segregation while small or rapidly cooled masses tend to show inverse segregation.

In addition to the two types of segregation described above, a third type known as gravity segregation may be mentioned. As the densities of skeleton crystals may be greater or less than the density of the liquid remaining after their formation, it follows that when these crystals are formed from isolated nuclei distributed throughout a melt they may tend either to sink or float upwards. When this occurs it is accompanied by a certain concentration of the first-formed solid either towards the top or the bottom of the ingot and the last-formed solid is therefore concentrated at the opposite end.

Since this section was written a review of the literature on inverse segregation has been published by Vaughan (608). In this will be found a survey of the experimental results obtained in investigations and a discussion of the theories that have been proposed to account for the phenomenon. Reference to this will show that the explanation based on the effects of feeding as described above is definitely the most acceptable. This explanation was first suggested by Bauer and Arndt, it has been accepted with or without modification by a number of subsequent workers, and it is supported by the recent work of Phillips and Brick (609).

OTHER ASPECTS OF CASTING

Some of the more important phenomena associated with the casting of metals have been described but many others are also involved. Thus in the filling of moulds of intricate shape the capacity of the metal for flowing is important, and this capacity, which has come to be termed 'castability', depends on a number of factors in addition to such obvious properties as viscosity and surface tension. In the solidification

of the metal and its subsequent behaviour, thermal conductivity, specific heat, latent heat of solidification, contraction on solidification, and strength at temperatures just below the freezing-point are important and have to be considered along with crystallization, selective freezing, feeding, and gas evolution. Even when attention is confined to the behaviour of the metals, the relations between the numerous factors involved are very complicated, and when variations in casting technique are also taken into account the subject becomes incapable of detailed description. For the present purpose casting technique may be considered to mean the size and shape of the mould, the type of mould, i.e. sand, metal or water cooled, the mould dressing, i.e. whether volatile or not, the number, size, and position of runners and feeders, and the temperature and rate at which the metal is run into the mould. It will be evident that a general description of the relations between the factors pertaining to the operation of casting and those pertaining to the behaviour of the metal cannot be undertaken, and most of what follows is intended primarily to describe the separate effects of the various factors, and to give some examples of the relations between certain groups of factors rather than to describe the casting process as a whole with reference to the mutual relations between all the factors.

Filling the Mould.

Three general aspects of this process may be considered: (1) the factors that affect the capacity of the metals for flowing, (2) how the molten metal run-in is distributed in the mould, and (3) the effect on solidification of molten metal running in while it is proceeding.

The first object in casting metals is to fill the mould with molten metal. There is no difficulty in doing this in the case of ingots or massive castings of simple shape, but when intricate castings with thin sections have to be made, difficulties in filling the mould may be encountered. Following the suggestion of Portevin the ability of a liquid metal to fill a mould is known as its 'castability'. This would seem in the first instance to depend on the viscosity of the liquid metal, but the viscosity as a physical constant of the molten metal does not vary much from metal to metal nor in a particular metal with the extent to which it is heated above the melting-point. The apparent viscosity, i.e. the reciprocal of castability, is mainly determined by other factors such as surface tension, the formation of oxide films, the presence of inclusions and incipient solidification. If, e.g., tenacious oxide films tend to form on the surface of the molten metal when it is exposed to the atmosphere, these will affect its ability to flow if the casting conditions permit them to form on the metal running into the mould. As inclusions in the molten metal are usually much more viscous than the metal, and may even be solid, its capacity for flow will tend to decrease as the quantity of these increases, and finally, once solid crystals begin to form they will clearly retard the flow of the metal.

Data are not available for the estimation of the castability of metals from knowledge of the factors on which this depends. Until recently, although several empirical tests had been devised and used, most of the knowledge on the subject was derived from qualitative practical observations. Following on the investigations of Guillet and Portevin (252) and Courty (253), however, a number of researches have been carried out in which an empirical method is used to determine the castability of different metals and alloys, the effect of casting temperature, mould temperature, &c., and to discover by inference the effect of such factors as range of solidification, &c. The details of the method of measuring castability are given in the papers mentioned above, and all that need be said here is that it is ascertained by feeding the molten metal under a constant head at the centre of a horizontal spiral cut in a metal mould, and finding the distance that the metal will run along the spiral. In general, the results obtained by the above investigators and by Portevin and Bastien (254) show that the castability of a given metal or alloy increases linearly with the difference between the melting-point and the casting temperature, i.e. with the degree of superheat. The slope of the line connecting castability and superheat varies, however, from metal to metal. The castability also increases linearly with the casting pressure, i.e. with the pressure exerted by the head under which the metal is flowing. Different relations exist, however, between castability and mould temperature, for as the mould temperature is raised above atmospheric the castability increases slowly at first, then more rapidly, and finally approaches infinity as the mould temperature approaches the freezing-point of the alloy. The curves connecting mould temperature and castability thus approximate to equilateral hyperbolae.

When the relations between castability and the composition of binary alloys are considered, a decision has to be reached whether equivalent conditions should be taken to mean a constant casting-temperature for all alloys, or one that varies with the composition so as to be the same amount above the liquidus in every case. Whichever of these methods is adopted, however, it appears that the castability decreases as the range of solidification increases, and is considerably less when the primary crystals grow by the formation of skeletons than when they grow as regular crystals of the type commonly formed by intermediate constituents and non-metallic elements. Thus Courty in studying the castability of aluminium-silicon alloys cast at 750° C. found that this decreased with silicon content up to 1.9 per cent. (the limit of solid solubility of silicon in aluminium under equilibrium conditions is 1.65 per cent., and this alloy has the widest range of solidification). Above 1.9 per cent. of silicon the castability began to improve as a result of the narrowing of the freezing-range as the eutectic composition (11.6 per cent. silicon) was approached. It did not attain a maximum, however, at the eutectic composition, but continued to improve with silicon

content up to about 20 per cent., thus indicating that although the freezing-range was increasing in width, the appearance of the primary crystals did not exert a controlling effect on castability because they did not grow as skeletons. Similar results were obtained by Portevin and Bastien with the alloys of lead and antimony, although in this case the casting temperature was maintained a constant interval above the liquidus. Beginning at the antimony end the castability decreased rapidly as the lead increased up to 10 per cent. (the limit of solid solubility in antimony), then it remained constant up to 60 per cent. of lead, increased from this point to a maximum at the eutectic point (87.5 per cent. of lead), and then decreased on the lead side of the eutectic. In this system neither of the constituents forms crystals of the non-skeleton type, but in the antimony-cadmium alloys a pronounced maximum on the castability-composition curve was obtained at the constituent SbCd which has a narrow freezing-range and forms regular crystals. An alloy of the composition of this constituent flowed 195 cm. along the spiral, while the pure metals antimony and cadmium flowed only 36 and 30 cm. respectively. The superior castability of alloys in which regular primary crystals form over those in which skeleton crystals form is due to the fact that crystals of the first type do not extend so rapidly and have not the same capacity for forming a solid network as those of the second type.

A factor associated with the filling of moulds that has an important bearing on certain aspects of the behaviour of metals in casting is the way in which the liquid metal run-in distributes itself in the mould. By pouring successive quantities of two alloys of similar properties but different colours, Genders (255) studied the way in which ingot moulds are filled by the stream of metal. The alloys used were a copper-zinc alloy containing 90 per cent. copper, and a nickel-silver alloy containing 50 per cent. copper, 30 per cent. zinc, and 20 per cent. nickel. These were poured in succession into a tun-dish, i.e. a trough of refractory material suspended above the mould, and containing one or more holes through which the metal runs into the mould. After solidification a longitudinal central slice was cut from the ingots, and the remainder was then divided transversely into eight equal parts. On polishing and etching the sections three zones of colour could be distinguished: (1) the red of the copper zinc, (2) the yellow of the mixed alloys, and (3) the white of the nickel silver. Various methods of pouring, i.e. top-pouring with a single hole, a single slot, and a 4-hole tun-dish, and bottom running with a 5-hole runner were investigated. Fig. 226 shows the results obtained in the experiments on top-pouring with a single stream. The diagrams on the right represent the distribution of the alloys on the vertical slice, those on the left the distribution on the eight horizontal sections examined, and the middle diagrams the distribution on a vertical section at right angles to the one on the right. The brass, which was poured first, is shown black, the zone of mixed alloys dotted, and

the nickel silver white. By pouring 25, 50, and 75 per cent. of brass various stages in the filling of the mould were recorded as shown in the figure.

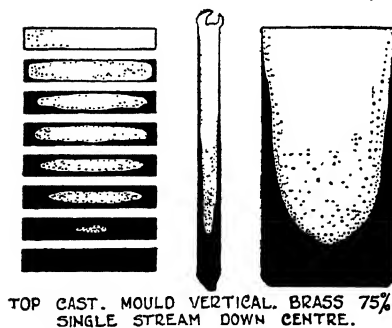
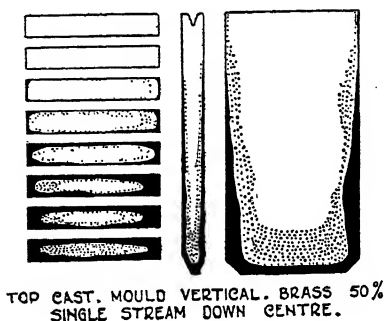
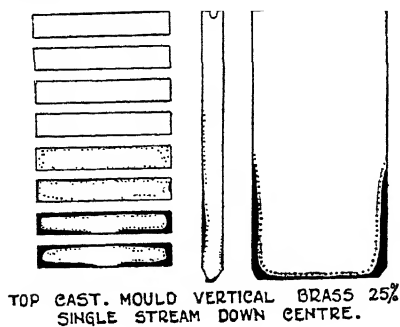


FIG. 226. Distribution of liquid metal in mould.

(*Journ. Inst. of Metals.*)

The results obtained in the other experiments using different methods of pouring were of the same general character as those illustrated in the figure. The principal conclusion to be drawn is that the metal which is first poured into the mould does not form the bottom layer. If freezing was almost instantaneous it would occupy this position, and the mould would be filled by the building-up of successive horizontal layers. When, however, the metal remains molten for some time after it enters the mould it is forced upwards and outwards by the incoming stream. Thus, under the conditions realized in Gender's experiments, the metal poured in after the mould was three-quarters filled penetrated nearly to the bottom, and traces of the metal forming the first 50 per cent. poured were forced up the sides nearly to the top. It is evident from this that while solidification was proceeding from the surface of the mould as a result of rapid abstraction of heat, a current of molten metal was flowing down the middle and up the sides. It is obvious that these results only apply exactly to the precise conditions under which they were obtained, but the general features indicated have a bearing on all casting operations and serve to show that turbulent conditions prevail while the mould is filling, and this must affect solidification going on at the same time.

The third factor to be taken into account in connexion with the filling of moulds is the relation of this to the process of solidification. If metal at a temperature considerably above its melting-point is poured rapidly into a mould that abstracts heat slowly, the mould may

be filled, and all turbulence due to the incoming stream may have ceased before any appreciable amount of solidification has taken place. In the absence of gas liberation from the metal, the mould, or the dressing, solidification will then proceed under quiet conditions such as those assumed in an earlier section in dealing with freezing in crucibles. At the other extreme, if metal at a temperature just above its melting-point is poured slowly into a mould that abstracts heat rapidly, freezing may keep pace with filling so that there is never more than a thin layer of liquid in the mould. In practice, however, the conditions actually realized are intermediate between the two cases just described. Solidification is proceeding as the mould is filling, but the relative rates of these two processes vary with the casting temperature, the rate of pouring, the heat-abstracting capacity of the mould and the size of the casting. As the rate of heat abstraction decreases with time as a result of the heating of the mould, the relations between filling and freezing will alter as they proceed.

If solidification is proceeding while the mould is filling, it is evident that the resulting turbulence will affect the process. In the first place, metal that is nearing its freezing-point is agitated by the incoming stream, and the formation of crystal nuclei is thus promoted. Furthermore, the currents set up flow over the surface of the crystals in the pasty range and may detach portions of skeletons which are carried away to serve as nuclei elsewhere. They also transport to other portions of the ingot liquid that has been enriched in solute or inclusions by selective freezing in the pasty range. Although the advance of the solid surface may approximate closely to what would be expected from a consideration of the abstraction of heat from a quiet liquid, the temperature distribution in the residual liquid will be greatly influenced by the incoming stream, and because of this new nuclei may appear in unexpected regions.

Solidification in Moulds.

The purpose of this section is to describe the effect on the macro-structure of cast metals of the conditions realized when they are poured into moulds and allowed to solidify. Attention will be directed primarily to the effect of factors other than those which operate during freezing in crucibles, and certain features of the casting process that have not so far been described will be dealt with briefly.

The molten metal poured into a mould may be supposed to be at a uniform temperature, and the change in temperature which it subsequently undergoes may be attributed to the effect of the abstraction of heat by the mould walls, modified by the effect of circulation of the melt, and the input of fresh molten metal while cooling and freezing are proceeding. The total time required to cool the whole mass of molten metal from the casting temperature to the freezing-point, and then through the range of solidification, is determined by the amount of heat

given up by the metal and the rate at which this can be taken up by the mould or dissipated through it. The amount of heat given up by the metal depends on its degree of superheat when cast, its specific heat, and its latent heat of solidification. The rate at which this is taken up by the mould depends in the first instance on its temperature, its capacity for absorbing heat, and the rate at which heat diffuses through it. When, however, a skin or shell of the cast metal has frozen on the walls of the mould, the thermal conductivity of this becomes a factor, and so does any air-gap formed by the contraction of this shell away from the mould. The total time required to freeze the metal is not, however, the only feature of importance, for the process of solidification is influenced to a large extent by the temperature gradients formed and the variation of these as freezing progresses. It is also influenced by the rate at which the metal in different parts of the mould cools through the freezing-range.

The three above-mentioned aspects of the freezing process are all related in that, if the metal, the mass, and the casting temperature are kept constant, the time taken to freeze the whole mass will decrease, while the temperature gradients, and the rates of cooling at different points will increase, with increase in the capacity of the mould for removing heat. When, however, metal, mass, casting temperature, and mould are varied it is necessary to consider each of the above aspects separately in order to appreciate the effect on the macrostructure of the general conditions of freezing.

The moulds used in casting metals may be divided into four classes, sand, steel or cast iron, copper, and water-cooled copper moulds. Sand being an insulator, moulds made of it give a slow rate of cooling and shallow temperature-gradients. The metal moulds of steel, cast iron, or copper give more rapid cooling and steeper temperature gradients, but their effect depends largely on their mass in relation to the amount of heat to be abstracted, and owing to the large difference in the thermal conductivity of the ferrous metals and copper respectively these two types must be distinguished. Water-cooled copper moulds give the most rapid cooling and differ from solid-metal moulds in that there is considerably less possibility of the initial rate of abstraction of heat undergoing a pronounced decrease such as occurs when a solid-metal mould has been heated to a certain temperature. The various types of moulds are not used as alternative ways of casting the same metal for the same purpose, but each has its typical applications. Sand moulds are used for the production of cast articles in all metals, and for this purpose they are only rivalled by metal moulds of steel or cast iron when the alloy and the article to be cast make die-casting possible. In the casting of ingots, bars, cakes, and slabs for subsequent remelting or working, cast-iron moulds were, until recently, almost exclusively employed, but in the non-ferrous metal industry, solid copper and water-cooled copper moulds have been used to an increasing extent since

about 1926. Cast-iron moulds are still used exclusively in casting steel ingots, but the use of bottomless moulds resting on a heavy copper-block or 'stool' is being tried and the practice is likely to extend.

Space will not permit a description of the cooling of different masses of different metals in different types of moulds, and in attempting a general description it is difficult to indicate how each feature of the cooling process is affected by all the variables concerned. In what follows, therefore, it is necessary to bear in mind that what is said about freezing in moulds while applicable to certain conditions cannot be applied without modification to others.

Sand moulds do not produce a marked chilling effect on the molten metal that comes into contact with their surface. The first layer of metal solidifies comparatively slowly and temperature gradients such as produce columnar crystals are not usually established. As the mould becomes heated up the rate of cooling decreases, and as this tends to promote the formation of larger crystals, the equiaxed crystals which are the principal type present in sand castings become larger as the distance from the surface increases. In solid-metal moulds the molten metal which comes into contact with the mould surface is frozen almost immediately, and the inner surface of the mould and newly formed skin of metal assume a common temperature. Heat then flows through the skin of frozen metal to the mould and from there into the mould. The rate of abstraction of heat from the molten metal and the pasty range now depends on its rate of diffusion through the solid skin and in the mould. Heat diffuses more rapidly through copper than through cast-iron moulds, and at this stage the rate of cooling in moulds of the former metal is more rapid than in those of the latter. In both types of mould, however, the rate of abstraction of heat falls off as the layer of solidified metal becomes thicker and the mould becomes hotter. This continues while the temperature gradient in the mould walls is decreasing rapidly, from the steep gradient established when the molten metal was first poured in to a much shallower and slowly changing gradient that is established when the conditions in the mould walls become steady and the heat flowing into the mould is balanced by that dissipated to the atmosphere from its outer surface. When this stage is reached the chilling effect of the mould may be said to be exhausted. The amount of metal that solidifies before this is the case increases with the mass of the mould, and is greater in the case of copper than of cast iron. If the mass of metal being cast is small in relation to that of the mould, the chilling effect will persist until solidification is completed ; but as the mass increases, the chilling effect becomes exhausted while larger and larger amounts of molten metal remain.

During the period of freezing when the mould is heating up and is exerting a chilling effect, small equiaxed (chill) crystals or columnar crystals are formed. When this effect is exhausted, however, the conditions in any liquid metal that remains tend to change over to those

that permit the growth of large equiaxed crystals from isolated nuclei. This change in the conditions is not entirely determined by the mould, but is also affected by the thickening of the shell of solid metal separating the metal from the mould, and by the formation of an air-gap between the inner surface of the mould and the outer surface of the ingot. These two surfaces are at first in contact and at the same temperature, but as the temperature of the remainder of the mould increases it expands away from the ingot skin. This results in the formation of an air-gap, which because of its low thermal conductivity causes a drop in the temperature of the inner surface of the mould and an increase in the temperature of the ingot skin. The formation of this gap has two important consequences. In the first place, the rate of abstraction of heat from the solidifying metal is decreased, and in the second the separation of the ingot from the mould surface leaves this thin layer of solid metal without support and sometimes it cracks. Several factors contribute to this. The formation of the insulating air-gap causes a rise in temperature and consequently an expansion of the skin. This tends to weaken it and to produce fissures. Furthermore, the separation of the mould surface from the ingot skin does not take place at the same instant over the whole ingot. Parts of the skin adhere to the mould while others become detached. This tends to stretch it and to cause rupture. If this separation begins when the skin is very thin, liquid metal flows out through the cracks giving rise to what is known as 'bleeding'.

During the chilling stage small equiaxed or columnar crystals are formed, and this mode of freezing may persist until solidification is complete. If, however, the mass of molten metal is great enough, then the change in the rate of abstraction of heat by the mould, the formation of an air-gap, and the increase in the thickness of metal between the pasty zone and the mould wall will produce conditions suitable for the formation of large equiaxed crystals growing from isolated nuclei. As this change-over depends on the temperature gradient falling below a certain value it is also affected by the casting temperature. The higher the temperature at which the metal is poured into the mould the steeper is the temperature gradient at all times during solidification. Consequently, the depth of penetration of the columnar crystals increases with the casting temperature. If this is high these will tend to extend to the centre of the ingot, whereas if it is close to the freezing-point none may be formed.


In addition to the factors pertaining to the abstraction of heat, the macrostructure of cast metals is affected by selective freezing as described in an earlier section, and by agitation resulting either from the liberation of gas from the metal or the mould dressing or from the filling of the mould. This agitation operates in two ways. Fragments from the thin skeletons in the pasty zone may be broken off and carried elsewhere to serve as nuclei, or alternatively the agitation may promote

the spontaneous appearance of nuclei. In either case the agitation tends to interrupt the gradual advance of solid from the surface towards the interior and thus to bring the growth of columnar crystals to a stop. At the same time it tends to increase the number of nuclei and hence to decrease the average crystal size. In consequence of this, metal from which gas is liberated, or which is poured under such conditions that solidification and pouring are proceeding concurrently, has smaller crystals than when it is cast under otherwise similar conditions without gas liberation or pouring during freezing.

If a mould is filled rapidly with metal at a high temperature, the effect of the turbulence resulting from pouring is a minimum because it has subsided before the metal, other than that in the chilled outer layer, has reached a temperature at which the appearance of nuclei can be promoted by agitation. As the casting temperature or rate of pouring is decreased, the effect of turbulence in initiating the appearance of new crystals becomes greater, because agitation goes on to an increasing extent in the metal near its freezing-range. Thus lowering the casting temperature or decreasing the rate of pouring tends to refine the crystal size. As an alternative to this the method of 'after-pouring' investigated by Hultgren (256) may be used. This method consists of pouring a small quantity of metal into the mould at a certain interval after the main pouring, and Hultgren studied the effect of this on small steel ingots 9 to 12 in. square. It was found that if the after-pouring was properly timed, so that the interior mass of molten steel was within the requisite range of temperature, a great number of nuclei appeared, and resulted in the formation of a system of small crystals in the interior portion of the ingot. If the after-pouring was too early no nuclei were formed in the interior of the mass, and if too late, crystallization had already begun at a few widely spaced nuclei and the after-pouring had little effect. Even when the after-pouring was performed too soon to initiate a shower of nuclei in the interior of the liquid it still affected the growth of the columnar crystals. In one experiment the growth of the columnar crystals from the surface was interrupted by this agitation and a zone of small crystals was formed. Owing to the high temperature-gradient still existing in the interior, however, a new crop of columnar crystals grew out of the equiaxed ones.

Fig. 227 shows a series of half longitudinal sections extending from the surface to the centre of ingots after-poured after different times compared with a similar section of an ingot not subjected to this treatment. The lines represent columnar crystals, the crosses the large equiaxed crystals formed in the absence of after-pouring, and the dots the small crystals caused by after-pouring. As solidification proceeds from the bottom towards the top as well as from the sides towards the centre, delay in after-pouring permits large equiaxed crystals to form near the bottom. Consideration of the sections shown in this figure indicates that the formation of equiaxed crystals begins at the bottom and

extends upwards, so that the zone of small crystals produced by after-pouring rises as the time of after-pouring is delayed. In each section the top of the ingot is occupied by large equiaxed crystals. The metal in this region was too hot at the time of after-pouring to be affected by the resulting turbulence. Its temperature was raised further by the new hot metal added. Consequently, it solidified later with the production of large equiaxed or semi-columnar crystals. It is evident from the results of these experiments that if pouring is proceeding after the metal in the interior of the mould has cooled to the temperature at which crystallization may be initiated by agitation, then small equiaxed crystals will be produced in the interior of the ingot. This condition is most likely to be realized if the casting temperature is low or the rate of pouring slow.

Agitation of the metal in the mould may also be caused by gas evolved from the metal or the mould dressing. It is a common practice to coat moulds with a substance which volatilizes and burns when the hot metal enters. This gives rise to a long reducing-flame that prevents oxidation of the incoming stream and of the surface of the metal in the mould. The gas resulting from the volatilization of this dressing bubbles up through the molten metal and has the same effect on the macrostructure as the liberation of large quantities of gas from solution in the metal. Genders (257) studied the effect of this on the macrostructure of brass ingots, and found that a fine equiaxed structure was produced in an ingot cast in a mould with a volatile dressing, while another ingot cast without a dressing, but under otherwise similar conditions, consisted mainly of columnar crystals with large equiaxed crystals in the interior. Similar results are obtained when ingots of metal cast with and without degasification are compared, and those in which substantial amounts of gas are liberated have a finer macrostructure than those in which this does not occur. Agitation by external means also refines the structure and has been used to some extent for this purpose. 

Contraction and Shrinkage.

As ordinarily used, the terms shrinkage and contraction have a similar meaning, but in connexion with the changes in volume of cast metals each is used in a special way. Shrinkage is used to denote the difference in volume between a cold casting and the mould in which it was made, i.e. it is the decrease in volume that must be allowed for in designing a mould in which to make a casting of specified dimensions. Other decreases in volume such as that which accompanies solidification are described as contraction.

If the castability of the metal and the design of the mould permit it to be filled with molten metal, then whatever the material of the mould a solid shell of metal will freeze on its surface. Thus irrespective of what subsequently occurs in the interior of the casting a solid shell that fills

the mould is produced in the first instance, and it is the change in volume of this during subsequent cooling that constitutes shrinkage which will thus be seen to depend primarily on solid contraction.

At the time of its formation or shortly afterwards the solid shell is filled with molten metal. As this cools to the freezing-point it contracts, and undergoes a further substantial contraction when it solidifies. The shrinkage of the solid shell is much smaller than the liquid-solid contraction that takes place in the enclosed metal, and consequently the amount of metal that will fill a shell when liquid is insufficient to fill it when solid. It is the great difference between the shrinkage of the shell and the contraction of the metal originally enclosed by it that gives rise to the formation of contraction cavities and the necessity for feeding. If each layer of solid that is formed while freezing is proceeding inwards from the solid shell is adequately fed from the remaining liquid, then the whole of the contraction that accompanies the cooling of the liquid and freezing will be concentrated in a cavity situated at the heat centre of the casting. If this centre, i.e. the last region to reach the freezing-point, can in turn be fed from an external source, then no contraction cavities will be produced in the casting proper. In so far, however, as each layer of solid is not adequately fed, small contraction-cavities will form, and in so far as the heat centre is not adequately fed large contraction-cavities will result. Arranging for proper feeding is therefore an important feature of casting technique.

Confining attention in the first place to the large contraction-cavities formed at the heat centre in the absence of proper external feeding, it may be said that the simplest example of this is the pipe formed in an ingot. In a steel ingot cast in a vertical cast-iron mould the solid shell is first formed on the sides and bottom of the mould, and freezing thereafter proceeds inwards and upwards. Owing to the contraction that takes place as the solid forms the level of the liquid in the mould gradually falls, and when solidification is complete the ingot contains a conical cavity at the top known as a pipe (Fig. 228). The depth of this pipe relative to the dimensions of the ingot depends on the magnitude of the contraction on solidification and the degree of superheat of the metal with which the mould is filled. McCance (258) has calculated that in a cylindrical steel ingot 50 in. high and 20 in. diam. the pipe would be 15 in. deep if the metal was cast with a superheat of 20° C., 17.6 in. if the superheat was 70° C., and 20.4 in. if it was 120° C. This applies to ingots with parallel sides, but in practice, to facilitate removal from the mould, steel ingots are cast in moulds with a slight taper. If the widest end is at the top the effect of the taper is to decrease the depth and increase the width of the pipe. If the narrowest end is at the top the effect is to increase the depth and decrease the width of the pipe. From the point of view of piping, moulds with the wide end up are the most satisfactory, but moulds with the narrow end up permit easiest removal of the ingots, i.e. 'stripping'. They are constructed in such a

way that the bottom consists of a slab of cast iron that is not attached to the walls, and stripping may be accomplished by lifting the mould with a crane.

The surface of the pipe cavity is contaminated with inclusions that



FIG. 228. Section of ingot showing pipe.

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rise out of the liquid metal or are rejected by the solid. It does not weld up during hot-working and must not be incorporated in any article made from the ingot. Three methods of avoiding this are now practised: (1) the portion of the ingot containing the pipe is cut off after a certain amount of rolling has been done, (2) the method of casting confines the

pipe to a feeder head which is not a part of the ingot and is subsequently cut off, (3) sufficient gas is permitted to be entrapped in the steel to compensate for contraction and prevent the formation of a pipe. The first method of preventing the incorporation of the piped portion in the finished article is used when killed, semi-killed, or balanced ingots (I, III, and IV, Fig. 225) are cast in moulds without feeder heads. The

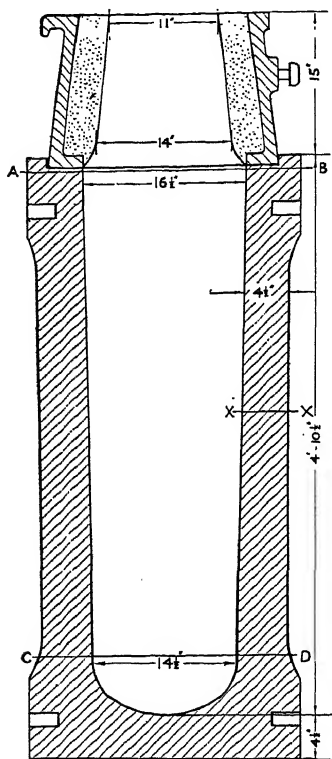


FIG. 229. Section of ingot mould with feeder head.

(*Journal of the Iron and Steel Institute.*)

second method is practised in the manufacture of good quality killed steel, and the third is utilized in the manufacture of rimming and rising steel (II, and IIc, Fig. 225). Fig. 229 shows a section through a mould with feeder head of the type now used almost universally in the casting of ingots of good quality killed steel. The main portion of the mould is of cast iron, and the section is particularly heavy near the bottom to promote freezing from the bottom towards the top. This portion, which is known as the chill portion, tapers downwards, and on top of it rests a removable refractory-lined portion which is the feeder head. When the mould is filled with molten metal, that in the head cools most slowly because of the refractory lining. Molten metal therefore feeds down and compensates for any contraction in the chill portion. At the end of solidification the pipe is localized in the head as shown in I, Fig. 225. The casting of ingots in moulds such as this involves more trouble in preparing the mould and removing the ingot than when simple moulds tapering towards the top are used. Consequently, moulds of this latter type are generally employed in casting ingots of ordinary

mild steel for general constructional purposes. If the steel is killed a substantial portion of the ingot must be scrapped (Fig. 228), but if the conditions are such that a semi-killed or balanced ingot (III and IV, Fig. 225) is produced there is less scrap, and if a rimming or rising ingot is made it can all be used.

The control of contraction cavities in sand castings depends on utilizing the same principles as in the casting of ingots. As far as possible the conditions are arranged so that the inevitable cavities will be localized in some unessential portion of the casting, i.e. in the feeder head. In order that this may be realized, solidification must begin at

points remote from the feeder head and proceed towards it in such a way that all the liquid metal is in contact with the head throughout the whole process of solidification. This is not easy to arrange in castings of intricate shape and variable cross-section, and the provision of the requisite number of feeder heads at the appropriate points in the casting is an important aspect of foundry technique. When the mould is ready to receive the metal, it consists of a cavity in sand corresponding to the casting required, plus additional space where reservoirs of molten metal may remain to feed the casting as solidification proceeds. The molten metal may be run in at one, two, or more points to fill the mould and the feeder heads. In order that these heads may be the last portion to solidify they must contain a relatively large mass of metal. Furthermore, in order that they may feed the casting satisfactorily they must be in immediate contact with the heaviest sections. In the comparatively simple case of a locomotive driving-wheel, a casting free from cavities should be obtained if a feeder head is placed over the three heavy parts of the wheel, i.e. (1) the hub, (2) the point of application of the crank, and (3) the eccentric balance-weight. This distribution of the heads will be efficient provided that the rim solidifies before the spokes. If, however, some of the spokes solidify completely at points between the rim and the feeder head before the solidification of the rim is complete, the contraction of the liquid thus cut off from the head will result in a cavity in the casting. This is a condition that may easily arise, for the mass of metal is relatively great just where the spokes are attached to the rim, and as freezing at these points may be slower than in the spokes, contraction cavities at the junction of the spokes and the rims are of common occurrence. In general, such cavities are due to inadequate feeding which may arise from insufficient or unsuitably disposed feeder-heads or because thick sections are fed through thinner ones. In order to overcome the difficulty of feeding it is sometimes necessary to place a 'chill' to accelerate the solidification of thick sections or to cast additional metal in the form of fins on thin sections.

Attention has so far been confined to the comparatively large cavities formed by the contraction on solidification of masses of metal as a whole. In addition to these, however, small contraction cavities may be formed round or in the interstices of dendrites due to inadequate feeding of the separate crystals. These cavities are of common occurrence in cast metals. They may occur at isolated points as a result of failure in the supply of liquid required to compensate for the contraction on crystallization, or they may be interspersed throughout considerable masses of metal due to the draining away of liquid before crystallization is complete. Their formation is closely related to the process of feeding as described in a previous section. This description was confined to solidification proceeding from the surface to the heat centre of an ingot, but much the same conditions arise when crystallization begins at isolated nuclei and the resulting crystals sink slowly through the melt.

In general, the liquid required for the final filling of the matrix of the skeletons at one point has to be drawn from the interstices of skeletons growing at another, and therefore adequate feeding involves the flow of metal through channels that become increasingly narrower as the skeletons become nearer to complete solids. At any point in a cast metal a contraction cavity may result from the closing of the channels through which it should be fed, but the occurrence of these cavities is most frequent where the greatest amount of feeding is required.

The flow of liquid metal towards growing crystals is promoted in the first instance by the reduction in pressure that arises from contraction where the crystals are forming. This tends to suck liquid to points where it is required. In ingots solidifying from the bottom and sides towards the top and centre the suction due to contraction is supplemented by the effect of gravity and the pressure of the overlying liquid. In certain regions in castings, however, solidification may be proceeding downwards, and gravity then tends to prevent feeding and must be counterbalanced by the pressure of metal in the feeder head. Besides promoting feeding the reduction in pressure that accompanies the contraction on solidification also facilitates the liberation of gas, and is probably the main factor determining the location of gas-holes in the interstices of skeletons and the boundaries between them. One of three things may therefore occur when contraction results in a reduction of pressure. Either liquid may be drawn in to feed the growing crystals, or gas may be liberated and prevent feeding, or neither feeding nor gas liberation may occur and a simple contraction cavity will result. Which of these occurs at a given point depends on the gas content of the metal and the freedom with which liquid may flow to prevent reduction in pressure.

As explained in dealing with inverse segregation, each successive layer of solid requires a greater amount of feeding liquid, for it must be fed with enough to replace that lost in feeding the previous layer and to compensate for its own contraction. As solidification proceeds therefore the demand for feeding-liquid becomes more and more pronounced, and in so far as its satisfaction is prevented by the narrow channels through which the liquid must flow, this demand tends to result in an increase in the number of gas and contraction cavities. Consequently, the porosity of ingots and castings tends to increase from the regions that solidify first to those that solidify last, and to reach a maximum in those latter regions from which liquid is drawn away to previously solidified portions and none remains to replace it.

The contraction of metal after solidification is complete is responsible for two types of defects of which the most common is hot cracks or tears. These are formed in newly solidified metal when the shape of the casting is such that the mould offers resistance to its contraction. When just solidified the metal is very weak and only a small stress is required to produce a crack or fracture. Such a stress may easily

be produced by the resistance of the mould to the contraction of the casting. If the whole casting solidifies and cools at about the same rate certain types of hot cracks may be avoided. Stress is not set up till the metal contracts, and it does not contract until it cools. Thus when the whole casting cools at the same rate, the stress that tends to produce the cracks and the strength to resist it develop together. The case is different, however, when certain parts of the casting cool before others. If, for example, a cylinder with a flange at each end and one in the middle is run at the middle flange, the portions of the cylinder adjacent to this flange will be the last to solidify. As the casting cools, its normal contraction is prevented by the end flanges being held firmly in the mould. Cracks are therefore liable to be produced in the hot metal near the middle flange. The contraction of metal on to cores is a frequent cause of hot cracks, and to avoid this type of defect collapsible or non-rigid cores are commonly used. Another common cause of hot cracks is a difference in section at different parts of the casting. The use of chills on heavy sections or of fins or temporary brackets on thin sections assist in avoiding cracks by producing equal rates of cooling.

Another type of defect caused by the contraction of the solid metal may be called 'cold cracks'. These are more rare. They are formed at a comparatively low temperature as a result of differences in temperature at different points. In the case of a thick section for example, cold cracks may be formed by the outer layer which is comparatively cold being expanded by the hot interior. Although cracks are rarely produced in this way, differential cooling may set up a condition of 'internal stress' which makes the metal more liable to fracture when external stress is applied. This phenomenon is dealt with more fully in the next chapter.

GENERAL CONSIDERATION OF CASTING

Throughout this chapter we have dealt with casting by isolating the more important phenomena and features and considering each separately in relation to certain closely connected factors. In any practical casting operation, however, the mutual relations between all the associated phenomena and conditions are concerned, and the consideration of all that may happen in such an operation may be a very complicated matter. In the first place, the mould must be filled with the metal and here the castability of the metal, the shape of the mould, and the material of which it is made come into play. Solidification begins at the surface of the mould and proceeds while filling is going on. At some stage between the beginning and the end of solidification gas evolution may begin, and from the point of view of the crystal structures of the casting, early gas evolution must be taken into account along with the turbulence due to filling as tending to refine the crystal size as a result of agitation. The tendency of agitation to cause the transport of liquid from

one part of the casting to another must also be considered. Under quiet conditions when there is no turbulence due to filling, and no gas evolution, the process of solidification is sufficiently complicated, involving as it does selective freezing, diffusion in the liquid, and feeding, and the relations between these determine whether normal or inverse segregation occurs and the number and distribution of contraction cavities. The formation of these in positions not in the pipe or feeder head is due to inadequate feeding, and they are frequently associated with late gas evolution, which is promoted by the same factors as feeding and tends to prevent it. Finally, after solidification is complete, solid contraction occurs and under certain conditions leads to hot tears and under all conditions to internal stress of varying intensity.

All the phenomena described in this chapter may be said to come into operation in casting generally, but their relative importance varies with the metal concerned, the size and shape of the casting, and the type of mould. In filling ingot moulds, for example, castability or fluidity is not of importance, and it only becomes so when intricate castings have to be made. Gas evolution also is of variable importance. Lead, tin, and zinc, and alloys based on them do not absorb gas or constituents that react to form gas, so that gas evolution is primarily a question affecting the casting of alloys based on iron, copper, and aluminium. Owing to the reducing conditions under which it is melted and its high carbon content, cast iron does not pick up sufficient oxygen to produce substantial amounts of gas during freezing. Steel being melted under oxidizing conditions does, but the methods of deoxidation are now fairly well understood and gas liberation may be prevented when it is undesirable. The volatility of the zinc in brass prevents gas absorption, and gas evolution is not an urgent problem in the casting of this metal. Copper and bronze, however, are very liable to porosity and to prevent it they have to be deoxidized, usually with phosphorus. As the gas responsible for porosity in aluminium alloys is hydrogen, which cannot be eliminated by making additions, this metal and its alloys are more difficult to degasify than iron and copper alloys, and some of the special methods of preventing porosity described in an earlier section have to be employed. The importance of the process of solidification and its relation to agitation also varies with the metal, the size of the casting, and the mould material. In small ingots or castings of non-ferrous metals made in metal moulds the whole of the metal is chilled. It may then consist of small equiaxed or columnar crystals and display only a small amount of segregation. As the size of the casting and the complexity of the alloy increases, the effects of the mechanism of solidification and related factors become more pronounced, and reach a maximum in the casting of steel in large quantities.

Although several references to casting temperature have been made, no section has been specifically devoted to this subject, and it is worth while to summarize its effects. For casting purposes a metal must be

heated to a temperature higher than that required to melt it, and the excess heat supplied is known as superheat. High melting-point metals lose heat more rapidly than low melting-point metals and therefore require more superheat, but this is also influenced by specific heat and thermal conductivity, and steel actually requires less superheat than copper alloys. The object of the superheat is to obtain the fluidity necessary to fill the mould, and the amount required therefore depends on the metal, the rate of pouring, the size and intricacy of the casting, and the material of the mould. Raising the casting temperature increases the castability and makes it possible to fill more intricate moulds and thin sections with a given metal. In this connexion there is, however, a great difference between one metal and another, and the castability of the various metals with suitable degrees of superheat is one of the factors that distinguishes good casting-metals from others. Thus the low castability of steel makes it a difficult metal to cast, while cast iron, aluminium-silicon alloys, and brass are easy to cast. The castability of some alloys is considerably increased by additions of certain elements. Thus a high proportion of phosphorus (up to about 1 per cent.) greatly increases the castability of cast iron, and lead has a similar effect in brass and bronze. While increased fluidity must in many cases be accounted an advantage derived from raising the casting temperature, the other effects are mainly detrimental, for it increases the amount of gas absorbed, augments the amount of contraction in the mould, which tends to increase the size of pipes and contraction cavities, and decreases the rate of cooling, which tends to increase the crystal size. The lower limit of the range of temperature from which a metal should be cast is determined by the amount of superheat necessary to fill the mould under given conditions of pouring, and in general higher temperatures than this should be avoided if possible.

In melting for casting, metals may be heated considerably above the casting temperature and subsequently allowed to cool before pouring. It is to be expected that such heating will increase gas absorption and accelerate any reactions taking place in the melt, but its influence on the macrostructure of the cast metal is not so evident. Nevertheless, it is now well known that 'superheating', as this is called, generally results in an increase in the crystal size of the cast metal. In certain cases, however, the opposite effect is obtained and this will be discussed in Chapter XIV in connexion with cast iron.

One further factor in casting may be mentioned, namely, the effect of oxide films formed on the metal in the crucible or the ladle or while running into the mould. Aluminium is the most conspicuous example of a metal on which tenacious oxide films are produced, and the casting of all alloys containing this metal is influenced by this property, even when the proportion of aluminium is as low as 2 per cent., which is the amount added to brass to increase its resistance to corrosion. When alloys containing aluminium are melted, a continuous oxide film is

formed on the surface. If this gets into the casting, as it commonly does when the metal is poured in the usual way over the lip of the crucible, it may prevent metal flowing into certain parts of the mould and may even produce discontinuities in the solid. So long as the molten metal is enclosed within the skin it behaves as if it were pasty rather than fluid. In order to control its behaviour a special method is sometimes used in casting such alloys. This is the Durville or rotary process. The mould is fixed above the crucible during melting, and when the metal is ready for casting the whole apparatus is rotated and the liquid runs into the mould leaving the oxide film in the crucible. Even ordinary brass develops oxide films if it is allowed to become oxidized prior to or during casting. These are responsible for surface defects in ingots and articles made from them, and oxidation of the metal during casting is usually prevented by the use of a volatile mould-dressing. As, however, other defects arise from its use, the British Non-Ferrous Metals Research Association have developed an alternative method of protection by means of an external gas-flame. More recently, however, the same association has shown that the oxidation of brass is prevented by the addition of about 0.04 per cent. of phosphorus. This element is gaseous at the temperature of the molten brass and forms a very volatile oxide which prevents the formation of a continuous oxide film.

Casting is the easiest way of shaping metal, but it is an operation in which many defects may arise, and a perfect casting is extremely difficult to obtain. Fortunately, many of the defects of casting can be eliminated by hot-working, and the casting of ingots which are subsequently worked to shape is resorted to whenever the best mechanical properties are required and the shape permits. There is no relationship between casting and working properties. Brass is very suitable for both casting and working, cast-iron and high-tin bronzes are easy to cast but cannot be worked, alloys of aluminium are to a large extent divided into two classes suitable for working and casting respectively, while steel is so difficult to cast that only about 2-2.5 per cent. of that produced is used without subsequent working. It is, of course, impossible to consider here how all the phenomena involved in casting operate during the casting of different alloys in moulds of different shapes, sizes, and materials. General accounts of the casting properties of different alloys are given in Parts V and VI, and for the present it will suffice to describe how the various factors in casting are related in one particular case, the casting of steel ingots.

STEEL INGOTS

There are at least three reasons to justify the selection of the casting of steel ingots as an example of the relations between the various phenomena involved in casting. In the first place, the amount of steel cast into ingot forms is many times greater than the total of all other castings.

Secondly, liquid steel contains a number of elements in solution, many inclusions, dissolved gases, and constituents that react to form gas; and as even quite small ingots are in effect comparatively large castings, they may be expected to display in a pronounced manner most of the phenomena associated with casting. Thirdly, steel ingots have been more thoroughly studied than any other type of castings. This is largely due to the work of the Heterogeneity of Steel Ingots Committee formed in May 1924, but numerous other investigations on the subject have been performed and references to these are given in the reports of the committee (259-65). Most of what follows is based on these reports considered in relation to what has previously been said in this chapter, but no attempt is made to summarize them and this section is not intended to do justice to the work of the committee. Rather is it intended to give an outline of the complexity of the subject they and others have undertaken to study.

The scheme of investigation employed by the Ingots Committee may be said to begin with the study of ingots of different sizes made from different types of steel. From this study certain information is obtained, and an effort is made to explain the different aspects of ingot structure in terms of the condition of the steel cast, the casting technique, and what is known about the phenomena of freezing, gas liberation, &c. In the course of endeavouring to reach an explanation it frequently becomes evident that satisfactory progress cannot be made in the absence of certain fundamental data, and researches to obtain this are put in hand. Thus the committee has sponsored investigations on the freezing temperatures of commercial steels, non-metallic inclusions, methods of determining oxygen content, gases in steel, the density of liquid steel, methods of determining the temperature of molten steel, the mathematical aspects of the cooling and freezing of ingots, &c. In the light of the information thus acquired the results obtained in the study of ingots are reconsidered. This scheme has not been followed in a historical sense, for attention has been given to each feature throughout the whole investigation. It is, however, the scheme that the committee has in mind and represents the logical development of the work.

The method employed in the study of steel ingots is to divide them vertically into two halves and then investigate the surface of one or both halves giving attention to (1) the general arrangement of crystals, i.e. the macrostructure, (2) the number and distribution of large gas-holes, i.e. the porosity, and (3) the distribution of the constituent elements and inclusions, i.e. the heterogeneity. For this purpose four methods are employed. For the study of heterogeneity, drillings may be taken at various points on the vertical section and analysed. This method is laborious and expensive, but it has been applied to many ingots by the committee and in some cases a large number of analyses have been made. An alternative method which gives an approximate idea of variations in sulphur content consists of taking sulphur prints,

and as the three segregating elements carbon, phosphorus, and sulphur segregate more or less together, although not to the same extent, this method gives a rough picture of general heterogeneity. These prints are obtained by pressing bromide paper soaked in dilute sulphuric acid on to the polished surface of the ingot section. The sulphuric acid reacts with the sulphur in the steel, hydrogen-sulphide gas is formed and reacts in turn with the silver bromide on the paper thus producing a dark stain of silver sulphide which varies in intensity from point to point with the sulphur content of the steel. To study the macrostructure the polished sections are etched with nitric acid, and besides revealing the arrangement of the crystals this method gives an idea of the heterogeneity, for regions where impurities are concentrated are attacked more rapidly and appear darker in colour than those which are relatively purer. The number, size, and distribution of large gas cavities may be studied by the naked eye, but in order to obtain a record of this, ink prints such as are described in an earlier section and shown in Fig. 225 are made.

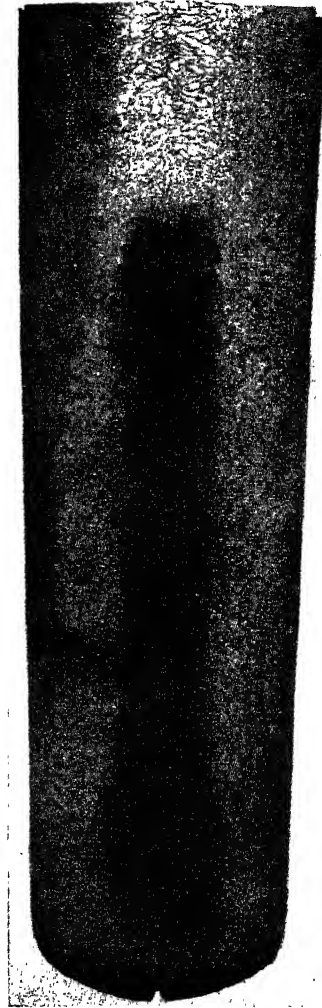
Macrostructure, heterogeneity, and porosity are all to some extent mutually related and depend on the appearance of nuclei, crystal growth, selective freezing, diffusion in the liquid, feeding, gas liberation, and the relations between filling and freezing. These are in turn related to the size, shape, and weight of the mould, the casting temperature, the rate of pouring, and the condition of the steel cast. The object of the work of the Ingots Committee is to establish the connexions between the factors so as to be able to say that a certain alteration in the condition of the steel or the casting temperature, &c., will produce a certain effect on the macrostructure, heterogeneity, and porosity by modifying the relations between the various aspects of freezing in a particular way. The programme of work in prospect indicates that this object is far from having been attained, and even if the work already done could provide an answer to all problems connected with steel ingots it would not be possible to include it here.

A certain amount of simplification is obtained by distinguishing between fully killed steel on the one hand and types from which substantial amounts of gas are evolved on the other. This distinction is made by the Ingots Committee throughout their work, and for the present purpose attention may be given in the first instance to the macrostructure of ingots of fully killed steel. Fig. 230 shows the macrostructure (after removal of feeder head) of vertical sections of two ingots of nickel-chromium steel cast from the same heat but at different temperatures. The average temperature during the teeming of Example 19 was about 1,590° C. and that of Example 20 was about 1,550° C. As photographs of etched sections do not reveal the details of the structure when considerably reduced, the pictures given in Fig. 230 were obtained by carefully tracing the outline of the crystals and photographing the drawings. Both ingots showed an outer skin of very small

equiaxed crystals produced when a layer of metal was chilled on to the mould surface. In the ingot cast at the higher temperature (Ex.19) a layer of columnar crystals grows inwards from the chill layer. Inside



Example 19.



Example 20.

FIG. 230. Macrographic structures in steel ingots.

(Reproduced by courtesy of the Iron and Steel Institute.)

the columnar crystals is a layer of fairly small equiaxed crystals, and in the centre of the ingot very small crystals are formed at the bottom and large ones at the top. The ingot cast at the lower temperature (Ex.20) differs from the other in that there are no columnar crystals, the region

of fairly small equiaxed crystals begins just inside the chill crystals, and in the centre the region of very small equiaxed crystals is much more extensive.

Comparison of the two ingots shown in Fig. 230 indicates the effect of casting temperature, and the differences between them can to a certain extent be accounted for on the basis of the influence of temperature gradients and the turbulence due to pouring as described in a previous section. The presence of columnar crystals in Example 19 and their absence from Example 20 are thus probably due to the steeper temperature gradients in the former than in the latter. In both ingots the small equiaxed crystals in the centre are probably formed as a result of the agitation promoted by the incoming stream. In the ingot cast at the lower temperature (Ex. 20) these extend farther towards the top, and this is probably due to the fact that in this case freezing had proceeded farther before teeming stopped. While these ingots show the general features of macrostructure, they can hardly be regarded as typical, and in most ingots the columnar crystals are a more conspicuous feature of the structure.

The elements in solution in liquid steel are carbon, manganese, silicon, and phosphorus. Some sulphur is also dissolved while the remainder exists in free globules of manganese and manganese-iron sulphides. In addition, the steel contains globules of oxides and silicates. All these constituents tend to segregate in the ingot. Silicon and manganese do not segregate to a very pronounced extent, and owing to analytical difficulties the segregation of the oxides and silicates has not been studied so thoroughly as that of the other constituents. Consequently, at the present time most of the information on segregation relates to the elements carbon, phosphorus, and sulphur. As a result of their studies of a large number of ingots the committee has shown that there is a kind of general scheme of segregation applicable to all ingots of killed steel. In the first place, the chilled outer zone does not differ greatly in composition from the molten metal cast, and in so far as it does so it tends to exhibit a slight concentration of impurities due to inverse segregation. The columnar crystals which grow inwards from the outer zone are purer than the average, and in this region normal segregation occurs. Inside the columnar crystals is a region of marked segregation in which the impurities are concentrated in stringers that slope from the ends of these crystals towards the top central position of the ingot. This is known as the Λ -segregate. In the axial portion of the ingot there is another region of segregation which extends from the top downwards, and in this region the impurities are concentrated in V-shaped zones. These Λ and V segregates are shown in Fig. 231 which is a photograph of an etched section and Fig. 232 which is a photograph of a sulphur print. In the region of the Λ and V segregates the concentration of impurities decreases from the top to the bottom and the bottom central portion of the ingot is the purest region.



FIG. 231. Etched section of steel ingot.
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In a complete study of the heterogeneity of an ingot many sampl

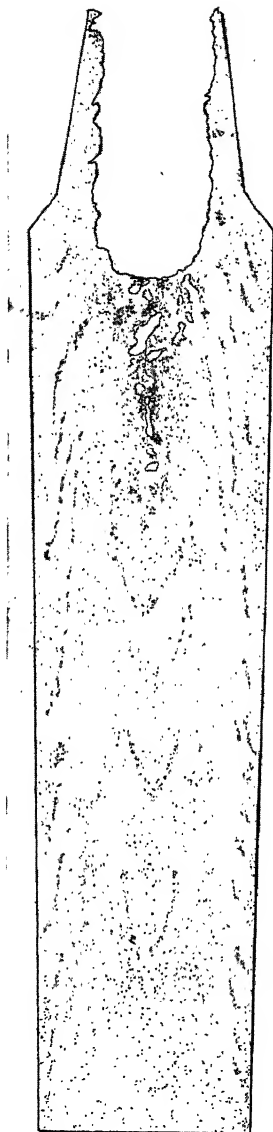


FIG. 232. Sulphur print of steel ingot.

(*Journal of the Iron and Steel Institute.*)

have to be analysed, but the committee has shown that a satisfactory measure of heterogeneity suitable for use in comparing ingots can be obtained by analysing samples from the seven points shown in Fig. 233. Point *A* represents the composition of the chilled outer layer which approximates most closely to that of the metal cast. *B* represents the composition of the relatively pure bottom central position, and *C*, *D*, and *E* show how the concentration of impurities in the axial region increases from the bottom to the top. *D* is within the usable portion of the ingot but *E* is in the head, which is discarded. Points *F* and *G* are in the intermediate zone of segregation, i.e. the Λ -region. The results of analyses taken at these reference points in nine ingots are summarized in Table 50. Taking the proportion of a given element in the liquid metal as 100 the figures given in columns 2 to 6 show how the concentration of the different elements varies from point to point. The figures in the last column indicate the variation in concentration of all the elements taken together. It will be seen that sulphur exhibits the most pronounced degree of segregation, and the other elements follow in the order phosphorus, carbon, silicon, manganese.

No steel ingot is completely homogeneous no matter how carefully it is made. In steel of a given composition the heterogeneity increases with the size of the ingot, with increase in the casting temperature, and with decrease in the chilling effect of the mould. In general, the degree of heterogeneity varies with the composition of the metal, the casting temperature, the rate of pouring, the size and shape of the ingot, and the design of the mould. Despite this, however, there are certain general features of segregation that are common to all ingots and these have been described above. It is more than probable that all aspects of segregation could be explained in terms of the phenomena already considered in this chapter, but the difficulty is to

TABLE 50

Average Composition of the Representative Ingots as shown by Analysis of Drilled Samples at the Selected Positions shown in Fig. 233

Position in the ingot as defined in Fig. 233.	Average figures for all the nine ingots					
	C	Mn	Si	S	P	All elements
E	141.8	103.9	107.7	148.8	134.8	127.4
G	112.1	103.4	101.8	115.1	118.4	110.2
D	106.8	100.9	101.8	114.2	108.7	106.5
F	104.6	100.7	104.2	101.3	106.0	103.4
A	103.8	100.6	100.7	99.0	104.0	101.6
C	94.7	97.7	101.3	88.0	93.8	95.1
B	85.7	97.2	103.0	76.6	86.7	89.8

assign to each its proper rôle. In the case of carbon, phosphorus, silicon, and manganese and such sulphur as is in solution in the liquid metal, the primary cause of segregation is selective freezing. In the case of such sulphur as exists in the form of free globules the primary cause is the rejection of these by the solid metal, and this acts in much the same way as selective freezing. As explained in dealing with solidification in crucibles and skeleton growth, the combination of selective freezing, diffusion in the liquid, and feeding may produce an ingot in which the concentration of impurities increases from the first portion to the last portion to solidify or it may produce one in which the conditions are reversed. In steel ingots of the sizes and types studied by the Ingots Committee the mechanism of freezing is such that normal segregation occurs, and consequently the concentration of impurities should increase from the bottom and sides towards the top and centre. This is approximately what occurs, and if solidification did not begin until the turbulence due to filling had subsided, if no gas evolution occurred, and if freezing took place progressively from the bottom and sides towards the top and centre it would be possible to

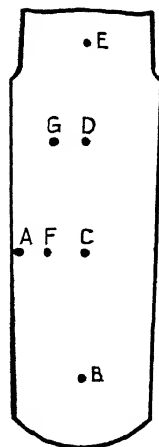


FIG. 233. Position of points for typical analyses of steel ingots.

account for the distribution of the impurities by taking account of the process of normal segregation and the progress of the freezing-point isotherm during solidification. In practice, however, numerous other factors intervene. Solidification begins concurrently with filling, and the incoming stream tends to displace molten metal from the bottom central region upwards and towards the sides. As the liquid displaced in this way has been concentrated in impurities by selective freezing beginning at the bottom, this process tends to increase the purity of the bottom central regions and decrease the purity elsewhere. Teeming is completed before freezing, but in the absence of accurate information

as to how these processes are related in any given case from the point of view of time, it is impossible to consider in detail the effect of the former on the latter or the effect of both on segregation. It appears, however, that in such of the liquid in the central zone as reaches its freezing-point before teeming is completed, small equiaxed crystals will form, whereas in the regions near the top where the liquid reaches the freezing-point after teeming is completed, large crystals will form. In any case, at a certain stage, free equiaxed crystals begin to form and progressive freezing from the sides and bottom is interfered with. The Λ -segregate is probably caused by upward-moving impure liquid being trapped in regions where free crystals are forming, and the V-segregate is probably caused by the downward movement of feeding-liquid when solidification is nearly complete.

CHAPTER X

HEAT AND MECHANICAL TREATMENT AND RELATED OPERATIONS

IN this chapter the operations performed on metals after they are cast will be considered mainly from the point of view of their effect on the metal and its properties. Thus, as in the consideration of casting, the plant used and the technique involved will be dealt with very briefly, while the general behaviour of the metals will be described more fully.

It is advisable to begin with a short account of the relations between the numerous operations comprising treatment, so that the connexion between the different sections of this chapter, and their relation to treatment in general will be clear. The operations concerned may in the first instance be classified under seven heads: (1) heat treatment, which for this purpose may be taken to mean all the heating and cooling operations to which the solid metal is subjected, (2) hot-working, i.e. all shaping operations performed in ranges of temperature in which recrystallization keeps pace with deformation, (3) cold-working, i.e. all shaping operations performed in ranges of temperature in which strain-hardening is produced by deformation, (4) de-scaling, i.e. operations performed to remove scale formed during heat treatment or hot-working, (5) machining (including grinding and polishing), (6) surface treatments, and (7) joining.

Each of the above general terms covers a varying number of operations which differ either in the way in which they are performed or in the purpose for which they are used. Thus heat treatment may be carried out to decrease the internal stress in a casting or a forging, to raise the metal to a temperature suitable for hot-working, to eliminate partly or completely the strain-hardening produced during cold-working, or to obtain the constitutional and structural state required for service or further treatment. Sometimes a particular treatment will achieve only one of these objects, but frequently it produces several effects, some of which may not be desired. Thus if an alloy that undergoes changes in the solid is heated for working, to relieve internal stress or to eliminate strain-hardening, its constitution and structure may be modified at the same time, and this modification may be either desirable or undesirable. Similarly, if it is heated and cooled under controlled conditions to modify its constitution and structure, the effect of previous cold work may be eliminated, and internal stress may be relieved or produced according to the heating temperature and the rate of cooling. The terms hot- and cold-working also cover a number of operations, which, however, are all performed with the same object, i.e. to shape the metal and produce such improvements in properties as come within

their scope. Hot-working comprises such processes as rolling, forging (under hammer or press), drop-forging (in stamp or press), and extrusion, while cold-working comprises rolling, stamping, pressing, drawing, and punching. De-scaling is performed either by pickling or abrasive blasting, but numerous different operations are covered by the terms machining, surface treatments, and joining, e.g. machining includes turning, milling, boring, planing, broaching, grinding, &c., surface treatments comprise tinning, galvanizing, carburizing, nitriding, anodizing, calorizing, electrodeposition, metal spraying, lacquering, and enameling, while joining covers welding, soldering, brazing, and riveting.

The numerous operations mentioned above may be combined in a very large number of ways to convert the castings first produced into the multitude of metal articles now required. If de-scaling, machining, surface treatment, and joining are left out of consideration in the first place, metals may be said to go into service (1) as cast, or cast and annealed to relieve internal stress, (2) as hot-worked, or hot-worked and annealed, (3) as cold-worked, or cold-worked and annealed to reduce strain-hardening, or (4) as finally heat treated after casting, hot-working, or cold-working to obtain the constitutional and structural condition required in service. These basic operations may in addition be combined in numerous ways with the others mentioned. Thus castings or hot-worked products may require de-scaling, de-scaling and machining, or de-scaling, machining, and surface treatment. Cold-worked articles require to be de-scaled before this operation begins, and after intermediate heat treatments unless these are carried out in inert atmospheres. After cold-working is complete they may then be machined or surface treated or both. Parts that are subjected to final heat treatments which produce great hardness (as when steels other than mild steel are hardened or hardened and tempered) have to be machined before this operation and finally ground afterwards. Sometimes, between the machining and the final heat treatment they have to be given a long heating at a comparatively low temperature to remove internal stress set up by machining.

It is quite outside the scope of this book to describe the sequence of operations performed in the manufacture of different parts from different alloys, and all that can be done is to consider the general features of the more important and most definitely metallurgical operations, namely, heat treatment and mechanical working. As already stated three aspects of each may be distinguished, plant, technique, and the effect on the metal, and the purpose of this chapter is to deal fully with the last aspect, while introducing enough about the others to show the general relations between all three.

INTERNAL STRESS

Internal stress may be developed during the cooling of castings or by mechanical treatment, and while some heat treatments eliminate

previously developed stress, others produce it. The phenomenon is therefore intimately connected with the subject of this chapter and it is worth while to consider it briefly. In general, internal stress is produced by (1) the development and change of temperature gradient during heating and cooling, (2) differential effects of working operations, and (3) volume changes accompanying constitutional transformations. Whenever a metal is heated or cooled, plastically deformed, or undergoes a phase change, some internal stress is developed, and this stress may under the appropriate conditions lead to spontaneous cracking or warping, either immediately or subsequently, to cracking or warping during machining, or to failure under abnormally low loads in service. In most metal components internal stress is undesirable, but it is intentionally produced in gun tubes and high-speed turbine rotors in order that the radial and tangential stresses imposed in service will be to some extent counterbalanced by internal stress of opposite sign. The production of such internal stresses is known as 'auto-fretage'.

The magnitude and distribution of the internal stresses induced in a given article by a particular treatment can rarely be calculated, and the experimental methods available for their determination leave much to be desired. In any case, the calculation or experimental determination of these stresses is a laborious and complicated operation and cannot be dealt with in detail. An excellent review of the methods of measuring internal stress has been prepared by Barrett (266), and the calculation of the stresses in gun barrels is dealt with by Macrae (267). For the present purpose, however, it will be sufficient to consider the phenomenon qualitatively with the object of explaining what it is and how it is produced.

Heyn (268) has illustrated the idea of internal stress by means of a system of springs. If three springs, of which two when released have the length l_1 , while the third has a greater length l_2 , are connected to cross-bars as shown in Fig. 234 the distance between the cross-bars will be less than l_2 and greater than l_1 . The shorter springs tend to pull the cross-bars closer together against the resistance of the longer. The shorter springs are therefore stressed in tension and the longer in compression, and the system is under internal stress such that the compression in the long spring balances the tension in the short ones. If the shorter springs were cut the distance between the cross-bars would increase, whereas if the longer spring were cut the distance would decrease. In the same way a balanced system of internal stress exists in a metal when the component parts are prevented from assuming their natural dimensions by the pressure of, or the necessity of maintaining cohesion with, surrounding parts. Should some part of the metal be cut away then the internal stress in neighbouring parts will be

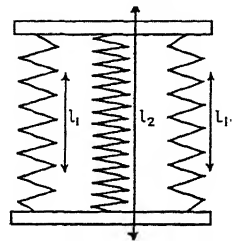


FIG. 234.

relieved and their dimensions will alter. Internal stress is therefore due to elastic strain or deformation produced in one part of a metal by the pressure or pull exerted on it by another.

A simple example of internal stress is provided by the cooling of a cylinder under conditions that lead to the development of substantial temperature gradients. Before cooling begins the cylinder is supposed to be at a uniform temperature and free from stress. Whenever cooling starts the outside cools before the inside, and owing to the temperature coefficient of contraction, the outside exerts a compressive stress on the inside, which in turn produces longitudinal and tangential tensile stress in the outside. Either of three things may then occur. If the relations between the temperature distribution and the elasticity of the material are such that the outer layers are not stressed beyond their elastic limit then they will return to their natural dimensions whenever they are permitted to do so. And if the stress imposed on the inner layers is also within their elastic limit they will likewise return to their natural dimensions. Before cooling began the natural dimensions of the outer layers were such as to include without stress the material of the inner layers, and the natural dimensions of the latter were such as to fill the space enclosed by the former. While a temperature gradient exists the outer layers are elastically stretched and the inner elastically compressed, but when cooling is complete and the whole cylinder has reached atmospheric temperature, then the conditions will be the same as when cooling began, i.e. the thermal contraction of the inner layers will have reduced them to the volume necessary to fill without stress the space enclosed by the outer. In this case, therefore, internal stress is temporarily developed while cooling is in progress but it disappears when the temperature gradient disappears.

Different results are obtained, however, when the outer layers are not capable of expanding elastically to the extent required to contain the remainder when the temperature gradient is a maximum. If, on the one hand, the outer layers are incapable of appreciable permanent deformation at the temperature they have reached when the temperature gradient is high, and if at the same time a substantial stretching of these layers is required to accommodate the hotter interior, then rupture of the outer layers will be produced. Again, however, if no permanent deformation of any part occurs during cooling the internal stress will disappear when the whole cylinder reaches the same temperature. If, on the other hand, the outer layers are capable of permanent deformation at the temperature they have reached when the gradient is steep, then the outward pressure of the hotter interior will tend to expand permanently the outer layers. When cooling is completed, therefore, the natural dimensions (i.e. not elastically stressed dimensions) of the expanded outside will be such as to enclose more space than is filled by the inside. Compressive stresses will then act on the outside and tensile stresses on the interior. The cylinder will then be

in a permanently stressed condition and internal cracks may be produced.

A metal is free from internal stress when the natural dimensions of each component part are such that it just occupies the space allotted to it by the surrounding parts. If this condition is not realized then each part will be maintained in a state of elastic stress by the pressure of, or its cohesion to, surrounding parts, and this is internal stress. If the metal is stress-free to begin with and is subjected to some treatment that elastically changes the dimensions of the component parts, then when the conditions realized in the treatment are removed, the metal will be restored to its original state except in so far as it has cracked during the treatment. If, however, the treatment permanently changes the dimensions of the component parts, then a condition of permanent internal stress is produced and persists until eliminated by a further treatment.

Several meanings may obviously be attached to the term 'component parts'. In the example given above these parts were taken as the outer and inner portions of a cylinder, but the component parts may equally well be regarded as separate crystals, groups of crystals or parts of crystals. In the case of elastic stress temporarily produced by a temperature gradient during cooling, it may be assumed that the tension is a maximum at the surface, passes through zero at some distance below the surface and reaches a maximum in compression at the centre. The internal-stress system is balanced throughout the cylinder as a whole and such a system is described as macroscopic. In the case of stress produced by a volume expansion resulting from a constitutional change, it is developed where the expanding phase is forming and is balanced locally. Such a system is described as microscopic. For the present we are concerned only with the macroscopic systems of stress, and the other type will be dealt with in Chapter XI, but it is necessary to refer here to the difference between them. In the examples just given macroscopic and microscopic systems are produced separately, but in general they are both produced at the same time. Thus if a constitutional change involving expansion or contraction does not proceed simultaneously throughout a given specimen, then macroscopic as well as microscopic stresses will be produced, and when permanent deformation occurs as the result of stress induced by a temperature gradient or mechanical working, microscopic stresses are produced as a result of the complicated mechanism of permanent deformation in addition to the macroscopic stresses produced by the differential effects of the working.

Before discussing the conditions under which internal stresses are produced and their practical consequences it is worth while to consider briefly some of the methods used in studying them. If a cylinder is free from longitudinal stress, its length will remain unchanged when metal is turned off the surface. If, however, it is in a condition of internal

stress a change in length will occur when metal is thus removed. If, for example, a thin layer is turned off the outside and the remainder then increases in length, it indicates that originally the layer removed was maintained in a condition of longitudinal tension by the remainder, while this in turn was maintained in a condition of longitudinal compression by the layer removed. Knowing the cross-sectional area of the part removed and of that remaining, and the modulus of elasticity of the material concerned, the internal stress can be calculated. This is the Heyn method, and Fig. 235 shows the result of its application to a

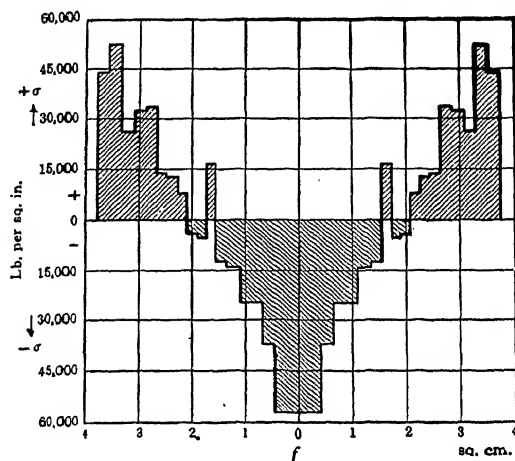


FIG. 235. Distribution of internal stress in cold drawn bar of 25 per cent. nickel steel.

(Heyn, *Physical Metallurgy*.)

rod of 25 per cent. nickel steel which had been cold drawn from 34 to 31 mm. diam. It will be seen that the internal stress varies from +53,000 lb. per sq. in. (tension) at the surface to -60,000 lb. per sq. in. (compression) at the centre. Thus before the outer layers were machined off, the natural length of these layers was less, and that of the inner layers more, than the actual length of the bar. Because of the cohesion between the component parts of the bar, the outside was maintained in longitudinal tension and the inside in longitudinal compression. When another similarly worked specimen of this bar was heated to 850° C. for about 30 minutes and slowly cooled (i.e. annealed) and analysed as above, the internal stress was found to have virtually disappeared. This is frequently the object of annealing treatments which promote the elimination of internal stress by permitting the component parts to deform permanently until they occupy without stress the space allotted to them.

Heyn's method permits only of the determination of longitudinal stress, but other methods have been developed for the measurement of radial and tangential stresses or of the complete three-dimensional

system. In measuring the radial and tangential stresses a series of circles is inscribed on the end of a cylinder and their diameters accurately measured. Then thin concentric rings containing those circles are cut out and the diameter of the circles again measured. In this way it is discovered whether the rings cut out, expand, or contract when removed from the constraint of the surrounding metal, and from the amount of this expansion or contraction the internal stress in the rings can be calculated. A method for the computation of internal stresses in three dimensions has been developed by Sachs (269). Successive layers are bored out from the inside of a tube or rod and the resultant change in length and external diameter of the remainder is accurately measured. From the data thus obtained the radial, tangential, and longitudinal stresses may be calculated. Other methods of measuring internal stress depend on determining the amount of springing of a strip cut from the specimen and several methods based on the study of X-ray reflections have been proposed.

By heating for a suitable time at a suitable temperature and cooling slowly it is always possible to obtain metals in such a condition that the internal stresses are small. This is the operation of annealing. Such treatment, however, generally results in the metal being obtained in its softest state and it cannot always be applied. For many purposes the strength and hardness required compel the use of metals that have been cold-worked or rapidly cooled and not subsequently annealed. In these conditions internal stresses of considerable intensity are liable to be developed. It will be evident from what has already been said that these stresses may result in distortion, change in dimensions, and cracking during machining. When their intensity is known and their direction is opposed to the stresses imposed in service, they may be used to advantage in service, as in the case of gun tubes, but when their intensity and direction are not known, service stresses may be superimposed on internal stresses with the result that safe working-stresses are unexpectedly exceeded. The present ignorance about the intensity and distribution of internal stress in many components is therefore the cause of some concern. In addition to the above effects, internal stresses may give rise to warping and cracking during heating operations or spontaneous warping or cracking some time after the completion of these operations. Finally, they have some very serious effects when certain metals in an internally stressed condition are exposed to corrosion.

Internal stress is produced during cold-working because of the differential effects of the working on the surface and interior layers respectively, and one of its best-known consequences is the phenomenon of 'season cracking'. Attention was first drawn to this in connexion with cold-worked brass when it was found that spontaneous inter-crystalline cracking could occur in this material without the application of appreciable external stress. Cracking of this kind occurred frequently

in cartridge cases, tubes, rods, bolts, screws, spun jars, cups, wire, and other cold-worked articles, and the time of its occurrence varied from a few weeks up to as long as fifty years after manufacture. Hence the term season cracking. On account of its practical importance this phenomenon has been the subject of several extensive investigations, and its occurrence, mechanism, and prevention have been carefully studied. It depends in the first instance on the existence of internal stress, but some other factor such as vibration, local or uneven temperature changes, oxidation or atmospheric corrosion, is required to initiate cracking, and the time that elapses before this occurs depends on the intensity of the internal stress and the effect of the other factors. One of the principal investigations in this field was that of Moore and Beckinsale (270) who found that season cracking, when promoted by the combination of internal stress and atmospheric corrosion, depended largely on the presence of small quantities of ammonia in the atmosphere. With large amounts of ammonia season cracking can be produced in a short time, and the same result is obtained by immersion in mercury, mercuric chloride, or mercurous nitrate. Immersion in a solution of the last-named salt produces rapid intercrystalline disintegration and is used as a test of susceptibility. Susceptibility to season cracking tends to decrease with the zinc content of the brass, and various limits of composition have been given as dividing susceptible from unsusceptible alloys. There are, however, no such definite lines of demarcation and all that may be said is that in general susceptibility decreases with zinc content. Season cracking does not occur when internally stressed brass is exposed to pure air. Small quantities of certain impurities such as ammonia, mentioned above, are required, and other substances which have the requisite effect are sodium chloride and acid fumes. As indicated by the effect of the test solution containing 1 per cent. of mercurous nitrate and 1 per cent. of nitric acid, which produces cracking in a few seconds or a few minutes, liquids are liable to be more rapid in their action than impure atmospheres. Thus, exposure to rain or a moist atmosphere that produces condensation accelerates the cracking, and if the lubricants used in the cold-working operation are contaminated with pickling liquid they will promote the defect. Susceptibility to season cracking may be eliminated by annealing, which relieves the internal stress. This treatment, however, also reduces the hardness resulting from cold-working, and when the strength and stiffness thus produced is required to be retained, the advantages and disadvantages of annealing have to be balanced. In general, the susceptibility to season cracking may be reduced substantially by annealing in the range 250–350° C. for 30 minutes, and the lower temperatures are used when retention of the cold-worked properties is regarded as very important while the higher temperatures are used when it is required to eliminate susceptibility to season cracking.

Season cracking of the type described above is not confined to brass,

but when we start to consider generally the occurrence of phenomena of this kind we enter a field where considerable uncertainty prevails. In the season cracking of brass three factors are outstanding: (1) the cracks or fractures are intercrystalline, (2) they are produced by the combination of internal stress and corrosive attack, and (3) only certain corroding agents have the specific effect required. There are, however, many other types of intercrystalline failure which when considered as a whole serve to show that all sorts of variations are possible in the conditions required to produce them. Copper, aluminium-bronze, aluminium, and steel have been shown to be subject to intercrystalline failure when in an internally stressed condition and subjected to certain kinds of corrosive attack. Thus internally stressed mild steel may crack when immersed in salt solutions, and cold-worked aluminium has been known to crack when immersed in certain kinds of water. External stress, may, however, have a similar effect. Thus when stressed steel is in contact with solutions of caustic alkalis or the nitrates of sodium, potassium, calcium, or ammonium it is liable to intercrystalline fracture. This has been the cause of many failures in chemical plant, and the 'caustic embrittlement' of boilers is due essentially to this phenomenon. Furthermore, when stressed steel comes into contact with molten brass, solder, or brazing metal, these are liable to penetrate along the crystal boundaries and cause disintegration, and similar effects have been observed with brass and other non-ferrous alloys. Sometimes, however, no stress at all appears to be required, as, for example, when duralumin undergoes intercrystalline corrosion in sea-water or lead cracks in lead acetate-nitric acid solutions. In both of these cases internal or external stress increases the severity of the attack, but it does not appear to be an absolutely essential factor.

In all the above-mentioned cases selective intercrystalline corrosion by a specific medium takes place. Under certain conditions this is sufficient to produce disintegration, but under others it must be assisted by internal or external stress. Clearly there must be some particular condition at crystal boundaries which causes this attack to take place. In connexion with the intercrystalline corrosion of austenitic stainless steel, the boundary condition responsible is known to be the removal of chromium from these regions, but in the cases mentioned above no peculiar boundary conditions are known to prevail. It is probable that in all metals and alloys there is some feature of the crystal boundaries that renders them susceptible to attack by specific agents. This susceptibility will vary, however, from metal to metal, and in a given metal with the composition and treatment. Many examples of intercrystalline failure have been observed, but it is likely that these are only a fraction of the number that would be detected if all the combinations of composition, treatment, corroding agent, stress, time, and temperature could be studied. Considering intercrystalline failure as a whole we may say that at one extreme there is the case of

the austenitic stainless steels in certain conditions (Chapter XII) in which only the boundary condition, time, temperature, and the corroding medium are concerned, and at the other extreme the case of the failure of metal under prolonged loads at elevated temperatures in which only stress, time, temperature, and the boundary condition are involved (Chapter IV). Between these, however, there are numerous examples in which both stress and corrosion are involved, and it is because internal stress may have the same effect as external stress that it is important in this connexion. A valuable review of intercrystalline failures has been published by Chaston (271).

Internal stress may be produced by hot-working as well as by cold-working, but because of the greater plasticity of the metal it is usually less intense. The stress produced during cold-working results from the differential effects of the working operations on the surface and interior layers respectively. This same factor comes into play during hot-working, but differences in temperature between the surface and the centre have also to be taken into account. If a billet that is being heated for forging is not kept long enough in the furnace for the interior to reach the same temperature as the outside, the outer layer will be more plastic than the interior, and this, combined with the natural effects of the working operations, will cause the outer layers to be deformed to a greater extent than the remainder, and internal stress will result. When the billet is uniformly heated throughout, the inside will cool less rapidly than the outside, and a temperature gradient in the opposite direction to the above will be established. In this case, however, the differences in plasticity due to temperature will tend to counteract the differential effect of the working, and the resulting internal stress should be less intense.

A common cause of internal stress is the development of temperature gradients during heating and cooling. If the three springs in Fig. 234 are replaced by three rods of equal length securely fastened to the cross-pieces, the system will be free from internal stress so long as the rods remain at the same temperature. If, however, the middle rod is heated while the two outer rods remain at the original temperature, its expansion will tend to push the cross-pieces farther apart against the resistance of the outer rods. Internal stress will then be developed in the system, the middle rod being in compression and the outer rods in tension. The intensity of the stress depends on the difference in temperature between the middle and outer rods, and on the temperature coefficient of expansion and modulus of elasticity of the material.

As the difference in temperature between the rods is increased the internal stress increases, but as long as the deformation produced by this is elastic, the rods return to the same length when the temperature difference disappears. All internal stress is thus eliminated. If, however, plastic deformation occurs, permanent internal stress is produced. In the case above described the elastic limit of the middle rod would

decrease as its temperature was raised and would therefore be reached before that of the unheated outer rods. Once this stress had been exceeded, further heating of the middle rod would result in plastic deformation and it would be permanently shortened. If it was then allowed to cool to the same temperature as the outer rods its natural length would be less than it was originally. Consequently, a permanent condition of internal stress would exist in the system, the middle rod being in tension and the outer ones in compression. The permanent stresses remaining after uniformity of temperature has been attained are therefore of opposite sign to the temporary stresses induced by the temperature differences. If the whole system in which the permanent internal stress has been produced is now heated into a range in which the rods become plastic, the internal stress will be relieved by permanent extension of the middle rod and permanent compression of the outer rods. If cooling is then carried out in such a way that the rods remain at the same temperature throughout the process, then the system will be free from stress at room temperature. This is the basis of annealing to relieve internal stress.

Although plastic deformation results in permanent internal stress in metals subjected to conditions producing temperature differences, it is a protection against rupture while the temperature differences exist. All stresses of thermal origin arise from the fact that the dimensions of metals increase with rise of temperature, so that if one part of an article is at a different temperature from another both parts must deform to accommodate themselves to the changed conditions. The resulting thermal stress is the stress corresponding to the required deformation. In an article of given dimensions subjected to a given thermal treatment, the amount of deformation that must take place to accommodate dimensional changes caused by temperature differences depends on the temperature coefficient of expansion. The stress developed by this deformation depends on the stress-strain curve of the material. Within the range of elasticity the relations between stress and strain are expressed by the modulus of elasticity. A high modulus means that a small increase in strain produces a large increase in stress. A low modulus means that a large increase in strain produces a small increase in stress. A material that is elastic almost up to its breaking-point and has a low modulus of elasticity could be subjected to fairly sudden changes in temperature without rupture. In metals, however, a high degree of elasticity is always associated with a high modulus, so that in hard or elastic metals, pronounced temperature differences between different parts produce very high stresses and easily lead to rupture. When, however, the metal undergoes a considerable amount of plastic deformation between the elastic limit and the breaking-point, the dimensional changes required to accommodate temperature differences may occur without danger of cracking.

In practice large differences in temperature between adjacent parts

do not arise, but gradual variations in temperature from outside to inside are produced during all heating and cooling operations, and sometimes also variations in temperature between different sides or between parts of different cross-section. If castings or forgings can be cooled or heated so slowly that the temperature remains substantially uniform throughout, no internal stress is developed; but as the rate of cooling or heating is increased temperature gradients are produced and internal stress results. The conditions that arise during the cooling of a cylinder have already been described, and it has been shown (1) that if all the deformation that occurs when the temperature gradient is high is elastic, then no internal stress remains when cooling is completed, (2) that if the metal is elastic up to near its breaking-point and substantial deformation is required by the thermal conditions, then surface cracks will form, and (3) that when permanent deformation occurs while the temperature gradient exists, then when cooling is complete a system of permanent internal stress remains. A pronounced difference must be noted, however, between the conditions prevailing at the surface and interior respectively. The stresses imposed on the outer layers are tensile. These layers tend to crack or expand and they are free to do so. In the interior, however, the stresses are compressive and are exerted in all directions. Now plastic deformation leads to a change in shape but not to an appreciable change in volume, and consequently if the stresses imposed on the interior are equal in all directions it will not be permanently deformed but only elastically compressed. From this point of view therefore all the changes that take place other than elastic deformation may be supposed to be confined to the surface layers which crack or expand in order to include the hotter interior.

The cracking or stretching of the outer layers of a cooling cylinder results from the fact that these layers are compelled to enclose a greater volume than they would have to if the whole cylinder was at a uniform temperature. There is, however, another way in which this result may be obtained, namely, by a change in the shape of the cylinder. The volume enclosed by a given surface area depends on its shape, and the ratio of surface area to volume is a minimum in a sphere. Therefore, when the outer layers are compelled to enclose a larger volume, they do so partly by stretching and partly by changing their shape to approach more nearly to that of a sphere. The cylinder becomes slightly barrel-shaped and the ends become convex outwards. It requires very rapid or repeated rapid cooling to produce a measurable change in shape, but under the appropriate conditions it can be obtained. As the interior must change its shape to conform with the surface, it follows that although the interior cannot be permanently compressed by stresses acting in all directions, it can be permanently deformed to give a smaller ratio of surface area to volume.

To the extent that the conditions produced by the temperature gradient are compensated for by a change in the shape of the cylinder no

permanent internal stress is produced, but in so far as they result in an absolute extension of the outer layers permanent internal stress exists when the whole attains a uniform temperature. Then the natural dimensions of the outer layers are such as to include a greater volume than that required to accommodate the interior. Consequently, the outer layers remain in a condition of elastic compression and the interior in elastic tension. It is in this condition that internal cracks may be produced.

During heating the surface layers rise in temperature more rapidly than the interior, and the surface therefore tends to expand away from the core. If the difference in temperature between the surface and the centre is sufficient the metal in the interior may be ruptured. As the core is being stretched in all directions by the expanding surface its capacity for plastic deformation does not decrease the danger of rupture, but the capacity of the surface for plastic deformation tends to decrease the stress in the core. Internal cracks produced by too rapid heating are known as 'clinks' and as the stresses produced by heating are in the same direction as those that remain after rapid cooling, rapid heating after rapid cooling is very liable to produce clinks.

In connexion with heating and cooling four aspects of internal stress may be recognized: (1) the development of stress by the temperature gradient, (2) cracking, (3) the production of permanent internal stress by permanent deformation, and (4) the elimination of internal stress by permanent deformation. During both heating and cooling internal stress may be developed. If elastic deformation only occurs this stress disappears with the temperature gradient; if the elastic deformation is accompanied by cracking the cracks remain when the stress disappears; while if permanent deformation occurs some internal stress remains. But the elimination of internal stress also depends on permanent deformation, and it must therefore be said that permanent internal stress is only produced when the conditions are such that plastic deformation occurs in one direction at a certain stage and cannot take place in the opposite direction at a later stage. Thus, when a specimen is cooled the outside is expanded when the temperature gradient is a maximum. Later, however, the temperature gradient slowly disappears, and if at this stage the outside is too rigid to be plastically contracted then internal stress will remain; if, however, the outside is still plastic while the temperature gradient is disappearing, then it will be permanently contracted and the production of residual stress will be wholly or partly prevented. This is what occurs during the cooling of soft metal. A similar phenomenon also occurs during heating, i.e. the outside is contracted while the temperature gradient exists, but owing to its increased plasticity it is easily expanded again to the requisite extent when the metal as a whole reaches a uniform temperature. It is because of this that permanent internal stress is not produced by heating, which actually serves to eliminate stress previously produced. It

will thus be seen that hard metals which have practically no capacity for permanent deformation tend to crack during heating or cooling rather than to develop residual internal stress, while soft metals which deform easily tend neither to crack nor develop internal stress, and it is thus the metals of intermediate hardness that exhibit the greatest tendency to be retained in a condition of internal stress after cooling.

Service failures may result from thermal stress particularly if this is repeated. Filling cold thick-walled vessels with hot liquors is an obvious cause of thermal stress, as is also the cooling of hot bearings by means of a water spray. Failures during manufacture are more common, however, for the preparation of metals for use involves heating and cooling through wide ranges of temperature during which pronounced gradients may be produced. The liability to failure by cracking increases with the hardness of the metal and the mass undergoing treatment. The greatest danger of cracking is therefore encountered in the treatment of ingots, castings, and fairly heavy forgings of steel other than mild steel. Usually large ingots of such steel are not allowed to cool, but are removed from the mould when just solid and transferred to a soaking pit where they are kept hot until ready for forging. Once the ingot has been reduced in cross-section and its structure consolidated by working there is less danger of cracking, and it may then be allowed to cool if necessary. Castings are not removed from the moulds at such an early stage in cooling as ingots, but usually they are broken out before the metal at the surface has cooled sufficiently to become susceptible to cracking. They are then transferred to the annealing furnace. By this means, cooling and heating through the dangerous range of temperature is avoided, and the final cooling in the annealing furnace can be made as slow as necessary. Castings or forgings that have been allowed to become cold should not be charged directly into a furnace already at a high temperature. They should either be heated with the furnace or else preheated in a furnace held at a lower temperature. In the case of very hard metals such as high-speed tool-steel, these precautions have to be observed even in the treatment of articles of fairly small section.

The effects of internal stress arising from constitutional changes in the metal are most pronounced in steel. As explained in Chapter VI, steel can be hardened by rapid cooling because the constitutional changes that take place above 650°C . during slow or moderately rapid cooling are suppressed by very rapid cooling. A different constitutional change then takes place in a range below 350°C . and results in the formation of a very hard constituent called martensite. In order to suppress the normal constitutional changes and obtain martensite in carbon steels they must be quenched in water, but the addition of nickel, manganese, chromium, or molybdenum makes it possible to obtain this hard constituent with less rapid cooling. In whatever way it is produced the formation of martensite takes place below 350°C . and is accompanied by an expansion.

The rate of cooling required to suppress the normal changes and retain martensite is known as the critical rate, and it varies with the composition of the steel and the temperature from which it is cooled. In a given specimen cooled by plunging into water or oil the rate of cooling is a maximum at the surface and a minimum at the centre and varies gradually through the intermediate regions. Under certain conditions of composition, size, and rate of cooling a specimen may be retained completely as martensite, under others martensite may be retained at the surface and the normal changes permitted to take place in the interior, and under others the normal changes may take place throughout.

The normal change from austenite to pearlite is accompanied by an expansion, but for the present purpose this may be neglected because it is so much smaller than that involved in the austenite to martensite change. If we neglect the ordinary thermal stresses that arise during the cooling of metals which undergo no constitutional change, and consider a cylinder of steel cooled at a rate that is sufficient to retain martensite throughout, we find the following conditions to arise. The temperature at which martensite can begin to form is first reached at the outside and it begins to expand. If this expansion could proceed freely, the volume enclosed by the surface when it had transformed to martensite would be sufficient to contain the interior without stress when it had also transformed. As, however, the expansion at the outside begins before that in the interior, a system of internal stress is established such that compressive stresses are exerted on the outside and tensile stresses on the interior. The compressive stresses on the outside tend to prevent its expansion, and in response to them the surface layer may deform so as to have less area than it would have if the transformation to martensite proceeded in the absence of compressive stress. Such contraction of the surface area cannot be measured, but it has been shown that the surface changes its shape so as to include less volume, i.e. the ratio of surface area to enclosed volume is increased by the surface and ends of the cylinder becoming slightly concave. By the time the formation of martensite in the outer layers is completed they have become too rigid to undergo further deformation, and they enclose less volume than will be occupied by the interior when it also changes to martensite. Thus, when the change is complete in the interior it tends to occupy more volume than is enclosed by the surface, which is therefore in tension while the interior is in compression.

The above account of the conditions that arise during the quenching of steel neglects several factors such as the effect of the normal coefficient of contraction and the fact that martensite may not be produced in the interior. Nevertheless, it explains the distribution of internal stress peculiar to quenched carbon steel and alloy steels cooled at slower rates but with sufficient rapidity to retain martensite. In contrast to metals which undergo no constitutional change involving

an expansion, the stresses developed in quenched steel when the temperature gradient is steep are compression at the surface and tension in the interior, whereas those developed when the temperature gradient is disappearing are tension at the surface and compression in the interior. Thus, whereas hard materials other than steel tend to crack soon after immersion in a quenching medium, steel exhibits no tendency to crack at this stage. This tendency develops later when martensite forms in the interior. Cracking may occur then, or at any time thereafter, and consequently quenched steel may crack at a late stage during the quenching operation, or subsequently. As will be explained in Part V, this cracking is frequently avoided by starting the tempering operation (i.e. heating to decompose the martensite) before the interior has cooled far enough into the martensite range to exert a dangerous pressure on the surface.

The decomposition of martensite during tempering is accompanied by a contraction, and it is evident that if a part consists of martensite throughout and the surface is in tension, then heating under conditions that cause the outside to temper before the interior will increase the intensity of the internal stress and promote cracking. One of the best-known instances of this is the production of surface cracks during the grinding of hardened steel, for the heat developed in grinding tempers the surface, intensifies the stress, and promotes cracking. The primary object of tempering is to wholly or partly decompose the martensite so as to reduce the hardness and increase the ductility of the steel, but it is also used to decrease the internal stress resulting from hardening. When a high hardness is required, tempering must be performed at a low temperature, and the internal stress is not greatly reduced, but as the tempering temperature is raised to obtain greater toughness and ductility the internal stress is progressively eliminated. To obtain maximum toughness, steels are usually tempered about 600–650° C. and this results in a substantial reduction in internal stress. There are, however, many types of steel that do not give a high notched-bar toughness unless they are rapidly cooled from the tempering temperature. This rapid cooling gives rise to a new system of internal stress, so that in obtaining high notched-bar toughness freedom from internal stress is to some extent sacrificed.

Although the foregoing explanation of the internal stresses developed in steel by the formation of martensite serves to account for many of the peculiarities of hardened steel, it must be pointed out that many factors that have a bearing on internal stress are left out of account. When, however, these other factors are introduced the subject becomes incapable of general consideration, for everything then depends on the balance between a number of related phenomena. By suitably combining the effects of these various phenomena it is possible to account for all kinds of variations from the typical behaviour described above, but for the present purpose it will be sufficient to indicate what these

phenomena are without endeavouring to explain the numerous ways in which they may combine in parts of different size and shape made from steels of different composition and cooled at different rates from different temperatures.

We have seen that when a metal that undergoes no constitutional change is cooled rapidly, the temperature gradient causes the outside to contract on the interior. In steel, however, the formation of martensite beginning at the outside tends to make it expand away from the interior. It would seem therefore that the effects of the ordinary thermal contraction and the martensitic expansion should tend to balance each other. Much depends, however, on the relations between the times at which these different factors become operative. If, for example, the formation of martensite at the outside were going on all the time this layer was cooling, then the expansion due to martensite formation would compensate, wholly or partly, for the thermal contraction, and tend to prevent the development of internal stress. Actually, however, the formation of martensite at the outside does not begin until it is cooled to a certain temperature which varies with the composition of the steel (Fig. 181, Chapter VI) but is usually below 350°C . Although, during quenching in water or oil, the outside is cooled from, say, 850° to 350°C . extremely rapidly, the fact remains that before the formation of martensite begins a condition arises when the outside is just above 350°C . and the interior just below 850°C . At this stage the outer layers will tend to stretch by plastic deformation of the austenite. Then, when the formation of martensite takes place they will stretch farther, and the tension exerted by the outside on the interior will be greater than if the outside had not been extended while in the austenitic condition. This will tend to decrease the permanent internal stress remaining after the whole specimen has transformed to martensite, and thus to decrease the danger of cracking, but it will increase the temporary internal stress existing while martensite is forming at the outside, and thus increase the amount of distortion.

When a specimen is first immersed in the cooling medium the surface is cooled rapidly to a low temperature and a maximum temperature gradient is established. Thereafter, the temperature at all parts falls gradually and the gradient becomes less and less steep. During this stage the temperature at the surface falls more slowly because the heat from the interior has to be abstracted through it, and it is difficult to say whether the outside passes through the martensite range more quickly, more slowly, or at the same rate as the inside does when it in turn reaches this range. The time taken to cool through the martensite range has little effect on the amount of martensite formed, but it does affect the amount of tempering that takes place. If the outside passes through the range more slowly than the interior it will undergo more tempering, and the tensile stress that is developed in the outside when cooling is complete will increase. If, however, the outside passes

through the range more quickly than the interior it will undergo less tempering, and the tensile stress developed in the outside when cooling is complete will be decreased. It is possible that variations in the steel, size of specimen, cooling medium, and initial temperature determine which of these occurs.

As the initial temperature and the rate of abstraction of heat by the cooling medium decrease, and the size of the specimen increases, the tendency for the normal changes to take place in the interior increases. As these involve less expansion than the formation of martensite, it follows that if a small region in the centre of a specimen undergoes the normal change, the tensile stress at the surface after cooling is complete will be less than if the whole had been retained as martensite. Furthermore, as the amount in the interior that undergoes the normal change increases, the tensile stress at the surface will decrease, and when a sufficient amount undergoes the normal changes the stress at the surface will change over to compression.

When the carbon content of steel is increased above 0.9 per cent. some austenite is retained unchanged by rapid cooling. The amount so retained increases with the carbon content, and in steel of any given carbon content the retention of increasing amounts of austenite can be effected by adding increasing amounts of nickel or manganese or of these elements plus chromium, molybdenum, &c. As the amount of retained austenite increases, steels tend to behave to an increasing extent like metals in which no constitutional change occurs, and when no decomposition of the austenite takes place, the behaviour of steel is similar to that of other metals, i.e. the surface is in tension when the temperature gradient is high and in compression when it disappears. It will thus be seen that the internal stresses temporarily or permanently induced in steel by rapid cooling depend in the first place on the volume expansion that accompanies the formation of martensite, but the effect of this is modified by the influence of thermal contraction, heat abstraction, the formation of constituents other than martensite, and the retention of austenite. As the composition of the steel, the size of the specimen, the initial temperature, and the rate of cooling are varied, the relative effects of these different factors also vary.

It follows from the above that if we consider a rapidly cooled steel to change completely to undecomposed martensite, and neglect the ordinary temperature gradient effects, then it follows that when the formation of martensite throughout the specimen is completed, the outer layers will be in tension and the core in compression. Surface cracking is therefore liable to occur when the austenite-martensite change in the interior is nearing completion, or at any time thereafter. If a specimen in this condition is heated, the outside will temper and contract before the inside, and the tension at the surface will increase. Thus, cracking is liable to occur during tempering unless the heating is slow, and it may also occur during grinding which heats the surface

layers. If the martensite in the outer layers decomposes during cooling to a greater extent than that in the interior, or if more austenite is retained at the surface than in the core, then the tensile stresses in the outer layers will be increased. These effects are unlikely, however, and in general, variations from the above-mentioned case of complete transformation to undecomposed martensite result in a decrease of the tensile stress at the surface. Thus, when the normal change takes place to some extent in the interior, or when more austenite is retained in the interior than at the surface, then the tension at the surface will tend to change to compression. The ordinary effects of the temperature gradient act in the same direction, and thus we may say that variations in the composition of the steel, the temperature of heating, the rate of cooling, and the size of the specimen are accompanied by changes in the internal stress at the surface which may vary from a high value in tension to a high value in compression.

The tempering of steel is carried out at temperatures below the critical range. If the tempering temperature is high enough, the internal stresses produced during previous rapid cooling will be relieved, and if the steel is now cooled slowly no appreciable stress will be produced. If, however, it is cooled rapidly, internal stress of the type produced by the temperature gradient effects will result, i.e. the residual stress at the surface will be compressive. In steels susceptible to temper-brittleness (Chapter XIII) rapid cooling after tempering is essential, and internal stress is thus produced. This may result in distortion either during heat treatment or subsequent machining, but it has also been shown to increase the fatigue limit in reversed bending tests. Thus, Bühler and Buchholtz (610) have shown that the development of surface compressive stresses by rapid cooling of steels containing 0.3–0.6 per cent. of carbon may raise the fatigue limit by about 20 per cent. This has been confirmed by Becker and Phillips (611). These investigators found that the surface compressive stress in a chrome-vanadium spring plate quenched after tempering at 700° C. was 37 tons per sq. in. The reverse bending fatigue limit of such stressed specimens was from 25 to 30 per cent. higher than that of unstressed specimens. In reversed bending tests it is the tension part of the cycle that brings about failure by the concentration of stress at the root of irregularities on the surface. When the surface is already in compression, however, the effect of the applied tension is decreased and the fatigue limit raised. There are, therefore, possibilities in the use of heat treatment to induce surface stresses that will counterbalance those imposed in service, but the subject has not yet been extensively studied.

In the quenching of aluminium alloys after solution treatment and before age-hardening, compressive surface stresses are again developed and their magnitude has been studied by Kempf, Hopkins, and Ivanso (612). In this investigation Sach's method of determining longitudinal, radial, and transverse stresses was applied to cylindrical specimens.

It was concluded that the stresses produced by commercial methods of heat treatment were of the same order of magnitude as the experimental error of the method, but under extreme conditions, involving quenching of heavy sections in iced water from higher temperatures than those used in practice, much higher stresses could be induced. The longitudinal stresses were found to be of greater magnitude than the tangential and radial.

GENERAL FEATURES OF HEAT TREATMENT

As explained in Chapter VI there are two general types of heat treatment, namely, those that are primarily intended to raise the metals to temperatures suitable for hot-working, to relieve internal stress or to eliminate the effects of cold-working, and those that are primarily intended to modify the constitution and structure of a metal by controlling the conditions under which changes in the solid state occur. Sometimes the term heat treatment is used to cover both types, and it is used in that sense here. But it is also used to refer specifically to treatments of the second type and was thus used in Chapter VI. It has long been customary, for example, to refer to hardened and tempered steel as heat-treated steel, and this usage has been extended to the non-ferrous metals so that a 'heat-treated aluminium alloy' means specifically an alloy that has been hardened by solution treatment and ageing. When convenient it is best to denote specific heat treatments by the special names attached to them and to use the term heat treatment to cover all thermal operations. This, however, is not always convenient and it is easier to say 'a heat-treatable nickel alloy' than to say 'a nickel alloy that is capable of being hardened by solution treatment and high-temperature ageing', but as a rule the sense in which the term is used is evident from the context.

In its general sense the term heat treatment covers a large variety of operations: e.g. the annealing of castings and forgings to relieve internal stress; the heating of ingots in preparation for working and the reheating of the numerous shapes produced from them at various stages during working; heat treatment before, during, and after cold-working; hardening and tempering, solution treatment and ageing; and finally heat treatment in connexion with surface-hardening operations. These treatments have to be performed on alloys of different composition, and on articles of different size and shape, and the details of the treatment vary with its purpose, the alloy, and the size and shape of the article. The resulting variations in plant and technique are innumerable, and it is impossible to deal particularly with the heat treatment of different products, from guns, boiler drums, and armour plates at one extreme to fine tools, springs, and fittings at the other. Certain features of the treatment of particular alloys and articles will be mentioned in this and succeeding chapters, but the principal object is to deal firstly with the factors that are concerned in all heat-treating operations, and

secondly with those that are generally concerned in operations of each type, e.g. the annealing of castings, heating for hot-working, &c.

Each heat-treating operation involves in the first place heating at a temperature that depends on the composition of the alloy and the purpose of the treatment. In some cases, slight variations in either direction from the selected temperature may have undesirable consequences and control must be exact, but in others, considerable variations in the heating temperatures may be permitted without appreciable alteration in their effects. Each operation also involves heating for a specified time which depends on the alloy, the purpose of the operation, and the size of the articles. In certain operations designed to produce hard surfaces on steel parts the duration of heating is very short, for the object is to raise the surface above the critical range as rapidly as possible by means of a flame or by high-frequency induction and to harden it by quenching without heating the rest of the component. Generally, however, the stock must be heated throughout, and while this involves no difficulty in the case of small stock, it requires prolonged heating in the case of large articles. If the object of the heating is preparation for working, the operation is completed when the ingot or partially shaped component is heated uniformly, or fairly uniformly throughout, but if the object is release of internal stress, annealing, the promotion of constitutional changes, or the alteration of the surface by causing some element to diffuse into it, then a further period of heating is required. The solution treatment of large aluminium-alloy castings, for example, requires a heating for several days as does the nitriding of steel.

Except in the case of ingots and castings transferred to a furnace while still hot, maintenance at the heating temperature is preceded by heating up. During this process, temporary internal stress, resulting in tension in the interior, is liable to be produced, and may give rise to the formation of internal cracks (clinks). The danger of this increases with the rate of heating, the hardness of the metal, and the size of the article, and to avoid it, too rapid heating must not be used. After the metal has been heated for the requisite time at the selected temperature or after the hot-working operations are completed, it must be cooled, and the rate of cooling is frequently important. If, for example, the object of the operation is to eliminate internal stress then cooling must be slow, whereas if it is designed to harden steel or retain CuAl_2 in solution in an aluminium-copper alloy it must be fast.

The satisfactory performance of a given operation involves, in the first place, knowing the correct time and temperature of heating, and the most suitable rates of heating and cooling in relation to the metal concerned, the size of the stock, and the object of the treatment. Secondly, it involves having a suitable furnace, charging the stock so that it will, as far as possible, be uniformly heated, and arranging for heating and cooling at the required rates. Thirdly, it involves adopting means

of determining, recording, and controlling temperatures and times. All these are essential factors in realizing the specific purposes of heat-treating operations, but in performing the treatments certain incidental features are introduced. Of these the most important is that the heated metal is exposed to atmospheres that may react with it and lead to trouble in service or subsequent processes. It is with the above features of heat treatment generally that the following sections are concerned.

Furnaces.

Every heat-treating operation requires some kind of furnace in which the heating or heating and cooling of the stock may be carried out, and in the metal industries many types are employed in performing different kinds of treatments on articles of different sizes consisting of one or other of the extensive range of metals and alloys in use. These furnaces may be classified in several ways, e.g. according to the method of heating used, the construction of the furnace, the nature of the operation performed, and the size and nature of the stock dealt with. No extensive description of furnaces is included in this book, which is concerned mainly with the behaviour of metals and only incidentally with the appliances used.

With regard to methods of heating it may be said that coke and coal are rarely used and that heat-treatment furnaces are usually fired with oil, gas, or pulverized coal or are electric furnaces. These last are at present used most extensively in the treatment of the smaller articles and the more expensive metals, but it is difficult to place any limit to their future employment, for at the present time they appear to possess several very important advantages that may be set against the higher cost per unit of heat generated. The cost of the necessary heat is, however, only one factor among many, and in the selection of furnaces the whole cost of heating, cooling, and handling of the stock must be taken into account and considered in relation to the quality of the product.

A heat-treating furnace may be described as a chamber in which the stock may be heated to the required temperature. In addition to this, however, it should be so designed that the temperature is uniform throughout the zone in which the stock is heated. As far as possible the heat generated should have free access to the whole surface of the articles being treated, and the stock should be placed in the furnace to allow of this. If the furnace is maintained at the correct temperature, if the distribution of heat is uniform, and if it has free access to every surface of the articles undergoing treatment, then it is only a matter of allowing sufficient time for the stock to be uniformly heated. There are probably no furnaces in which these conditions are completely realized, but there are some in which they are approached very nearly. In general, however, heat-treating furnaces vary considerably in the accuracy with which the temperature is controlled and in the distribution of heat in the charge.

Heat is very difficult to control, and its application in such a way that charges of different kinds may be uniformly affected raises many problems in the design of furnaces and the packing of stock. In fuel-fired furnaces heat is conveyed to the stock by the hot gases produced by the combustion of the fuel, and there are several ways in which this transference may be effected. The simplest and most economical method from the point of view of thermal efficiency is when the hot gases circulate about the charge and heat it directly, but variations in the uniformity of the heating are obtained in this way. If the furnace is designed and the charge is disposed so that the hot gases entering the heating chamber do not impinge against one portion of the stock but circulate slowly around it all, then fairly uniform heating may be obtained. If, however, the hot gases impinge against the charge and then escape to the flue, uniform heating does not result. In other fuel-fired furnaces heating is effected by radiation, and there is less danger of unequal heating. In many furnaces of this type the hot gases pass through the chamber in which the stock is contained, but the direction of their flow is such that they pass over and round the stock, which is heated by radiation from the gases and from the heated walls and roof. In another form, known as the muffle furnace, the gases are confined to flues outside the chamber containing the stock. In electric heat-treating furnaces the heat is generated by passing an electric current through 'resistors' which transfer the heat produced to the stock by radiation. Resistors made of heat-resisting alloys such as the nickel-chromium alloys can be used when furnace temperatures up to about $1,000^{\circ}\text{C}$. are required, while higher temperatures up to $1,250^{\circ}\text{C}$. may be obtained by using resistors made of silicon-carbide. The application of heat to the charge is controlled by the disposition of the resistors. These may be placed either under the hearth or on the walls or roof of the heating chamber, or in all three positions; and since they can be made to radiate the necessary amount of heat, this type of furnace gives a more positive control of the distribution of heat than any of the fuel-fired types.

Furnaces in which the stock is packed, heated to the necessary temperature, and then withdrawn, are known as 'batch' furnaces. Such furnaces are intermittent in their working, and there are two ways in which they may be operated, viz. either they may be maintained at the working temperature and the stock charged and withdrawn as required, or they may be cooled each time for a fresh charge to be inserted and heated with the furnace. The former method of working is naturally the more economical and is used in all cases where the size and mechanical properties of the articles being treated do not make it dangerous to place them directly in a furnace held at the temperature to which they have ultimately to be heated. This method cannot be used, however, in annealing large steel castings, in heating high-carbon or alloy steels for forging, or in heating high-speed steels before quenching. In all these cases internal cracks would be liable to result from the thermal stresses

set up when the metal was placed in a furnace held at a high temperature. To avoid this danger the furnace must be cooled before the charge is put in, or else the charge must be first heated to a lower temperature in a preheating furnace. The second alternative is the more economical and convenient, and is almost invariably used in the heating of tools and other parts made from high-speed steel. Heating the charge with the furnace, must, however, be resorted to in heating cold billets of high-carbon or alloy steel if they are more than 12 inches square, and also in heating large steel castings.

In heating metals for hot-working, the billets are subsequently withdrawn from the furnace at the working temperature and cool as they are worked, while in other types of heat treatment free cooling in air or quenching in water, oil, molten salts or molten metals are essential parts of the process. In certain operations, however, slow cooling is essential. Parts made of air-hardening steel must not be allowed to cool in air at any intermediate stage in the working operations because of the danger of cracking, and slow cooling is an essential feature of the softening of metals by annealing. The air hardening of steel may be prevented by transferring the forgings to a furnace at 600° C. for a certain length of time to enable the normal constitutional changes to take place, but in annealing operations it is slow rather than delayed cooling that is required. When the 'batch' type of furnace is used, this is obtained by packing small articles in boxes in which they are heated and cooled, but in certain processes the furnace is allowed to cool with the charge.

In furnaces of the batch type, light stock is charged and withdrawn by means of tongs, while heavy stock may be handled in several ways. In the soaking pits used for heating ingots, charging and discharging is done through doors in the top by means of a crane. In the furnaces used for heating slabs and billets various types of chargers which insert and withdraw the stock through side-doors are used, and very heavy stock such as armour plate is usually heated in 'car bottom' furnaces in which the hearth is mounted on wheels that run on rails so that the charge is carried in and out of the furnace on the hearth.

Several advantages are obtained by using continuous furnaces in which the stock is moved through the furnace by a suitable mechanism. In these the duration of heating is controlled, but their use is restricted to work in which there is a regular production of articles undergoing the same treatment. As such a large proportion of industry now works on a mass-production basis this is not a very serious restriction, and the use of these furnaces is extending rapidly. One of the oldest types of continuous furnace is that used for heating wire rod. This rod comes from the hot rolls in coils which are placed on a drum and drawn through the furnace by a drum at the other end. The back end of one coil is attached to the front end of the next one, and the process is therefore continuous. When it is necessary to cool the rod in some medium other

than air, e.g. molten lead, a system of rollers leads it into the quenching bath on emerging from the furnace. On leaving this it winds on to the drum that supplies the pull. Another early type of continuous furnace is the 'pusher' furnace in which a hydraulic ram pushes boxes or billets in at one end, and each box or billet progresses along the furnace as fresh stock is inserted. Recent improvements in heat-resisting alloys have made it possible to construct furnaces with more elaborate mechanisms for moving the stock. Three such furnaces are illustrated

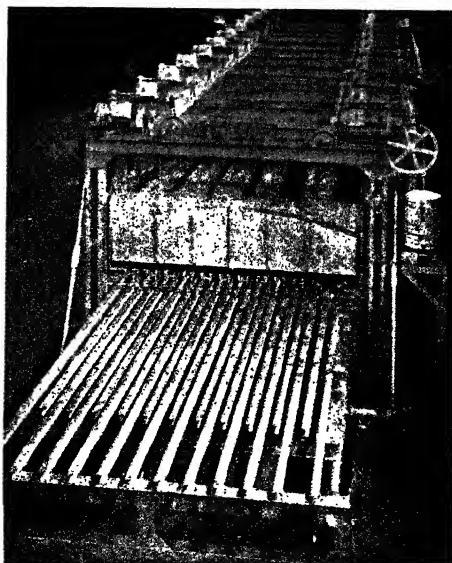


FIG. 236. Sheet-normalizing furnace with walking beam conveyer hearth.

(*Metal Progress.*)

in Figs. 236-8. The first shows a large furnace used for normalizing steel sheets in which the sheets are transported along its length by a 'walking beam' conveyer, the second shows a slab conveyer in a furnace used for heat treating small parts, while the third shows a roller hearth furnace used for annealing tubes. In a rotary furnace the charge moves round a circular furnace on a moving hearth or on arms suspended from above.

One advantage of conveyer furnaces is that they can be placed in the production line and constructed so as to keep pace with the other operations in the plant. The time of heating is controlled by the rate of the conveyer and all stock receives the same treatment. When it is necessary to quench the stock in oil or other media it can pass directly from the furnace into the quenching bath and out again, and in fact such furnaces can be made into automatic heat-treating machines. By arranging the supply of heat they can be made to heat the stock slowly

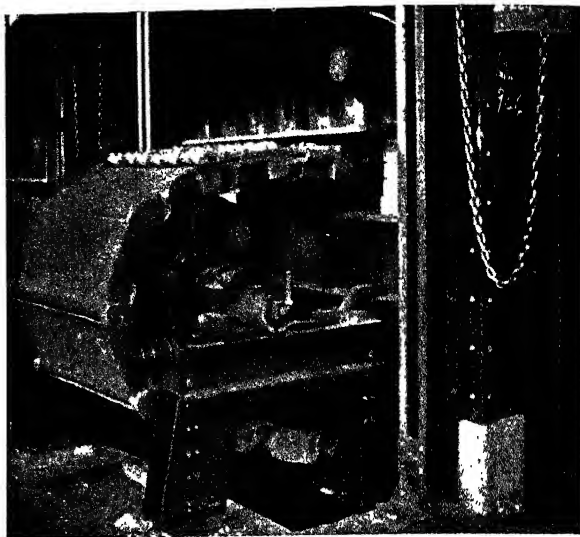


FIG. 237. Furnace with slab conveyer hearth.
(*Metal Progress.*)

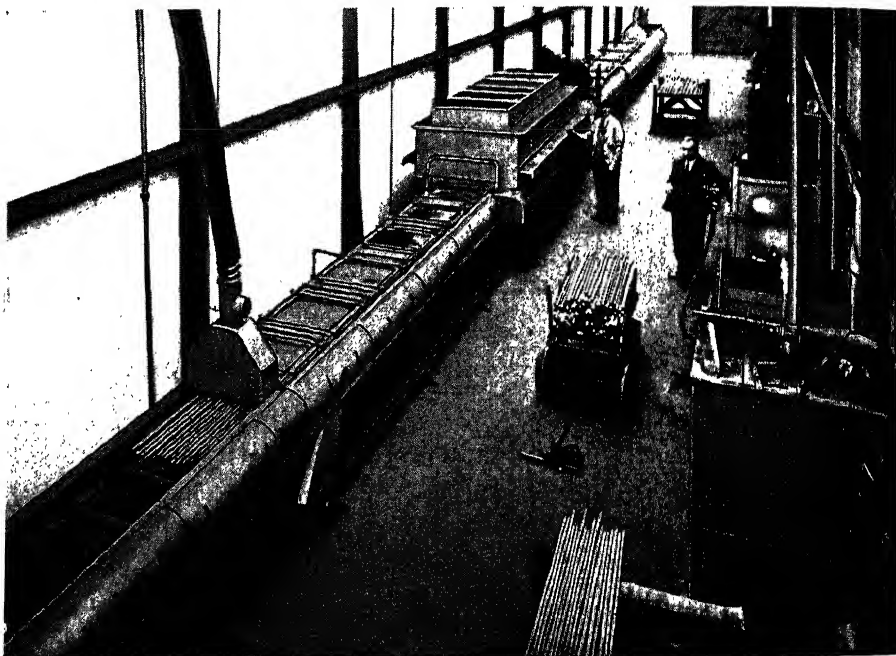


FIG. 238. Roller hearth furnace for annealing tubes.
(*Metal Treatment.*)

as it enters at one end and cool it slowly as it leaves at the other. This is most easily arranged in electric furnaces, but it can also be provided for in gas- and oil-fired furnaces. In furnaces of the latter type the spent gases from the hottest zone are used to heat the preheating and cooling zones. Recuperation is therefore obtained without recuperators and substantial economies are effected.

For certain purposes direct resistance heating may be used. Thus a machine has been described for hardening hacksaw blades of high-speed steel by passing a current through them until they reach the requisite temperature, then switching off the current and allowing the blades to cool in air. Owing to the small section and the composition of the steel, this cooling is rapid enough to produce hardening. Other applications of this method are in the heating of wire rod and wire, tubes, bars, and rivets. Another method of heating which is described more fully in a later section consists of immersing the stock in a bath of molten lead or molten salt maintained at the requisite temperature.

Factors in Heat-treating Operations.

Furnaces and their accessories constitute the heat-treatment plant. The phenomena involved consist of the reactions between metals and furnace atmospheres, which are considered in the next section, and the effects of heating and cooling on the metals, which are discussed in relation to particular operations in later sections. In the meantime heat-treatment technique, which consists of arranging and controlling the heating and cooling cycles, may be considered briefly. This is a subject that is not very suitable for general discussion because temperatures, times, and rates of heating and cooling vary with the purpose of the treatment, the composition of the metal, and the dimensions of the articles. For this reason only the most general consideration is possible at present.

Most heat-treating operations give satisfactory results only when the stock is heated within fairly narrow temperature limits. Consequently, in arranging a treatment the most suitable temperature must be selected and provision made for its control. The factors that are taken into account in selecting the temperature vary with the purpose of the operation and the composition of the metal, as do the consequences of exceeding or failing to reach the correct temperature. Annealing of castings to relieve internal stress is practically confined to castings in steel or cast iron, and in both of these types of alloys the selection of the annealing temperature cannot be considered without regard to the possible constitutional changes. Thus iron castings are annealed in the range 440–520° C. (for from 30 min. to 5 hours according to their section) because lower temperatures would not relieve the stresses, and higher temperatures would weaken the metal by allowing cementite to change to graphite as described in Chapter XIV. In annealing steel castings, however, it is desired to refine the crystal size in addition

to relieving internal stress, and these are consequently heated well above the critical range (line *GSE*, Fig. 168), i.e. to about 920° C. when they contain 0.15 per cent. of carbon and 840° C. when they contain 0.6 per cent.

Many metals are hot-worked and have to be previously heated, but those most commonly treated in this way are steel and certain aluminium alloys. As the plasticity of metals increases with temperature, and as this increase is very rapid when the melting-point is approached, hot-working is facilitated by heating to the highest possible temperature, especially when the alloy is inclined to be stiff or the mass to be deformed is large. As opposed to this advantage, however, high temperatures are liable to result in 'overheating' or 'burning', and in the case of steel and copper alloys, excessive scale formation. Overheating is a term applied particularly to steel and it means that excessively large austenite grains have been produced during the heating operation. What constitutes an overheated structure varies, however, with the object of the treatment, and a casting or forging may be said to be overheated during annealing although the austenite grain size produced is less than that normally obtained in heating for hot-working. The size of the grains produced during heating is only one of many factors that influence the final structure of the worked metal, and in connexion with this, account must be taken of the amount of working subsequently performed, the rate of this working, the temperature at which it is stopped, and the subsequent rate of cooling. Nevertheless, very large austenite grains produced during heating for working tend to result in a coarser final structure, and also to make the metal more tender and liable to fracture during working. Burning is applied more generally and signifies that the heating temperature has been so high that the cohesion between the crystals has been weakened or destroyed and the metal made susceptible to fracture during working or in service. This phenomenon will be considered later; meanwhile, it may be said that it is not due to one factor, but is the result of different combinations of weakening of intercrystalline cohesion at temperatures near the melting-point, fusion of low melting-point constituents, and formation of oxide films round grain boundaries. In any case the correct temperature of heating in preparation for working has to be selected so that the metal will be sufficiently plastic to respond to the particular operation without any danger of burning being incurred.

Heat treatment after working in order to eliminate internal stress and refine the crystal size is an operation that is almost entirely confined to steel and is called normalizing. As the finest crystal size is obtained by heating just above the critical range (line *GSE* Fig. 168), the heating temperature is kept as close to this as is consistent with ensuring that the whole mass is heated above the range. Thus carbon steels containing from 0.1 to 0.2 per cent. of carbon are normalized at about 920° C., those containing from 0.3 to 0.4 per cent. about 880° C. and those containing

from 0.5 to 0.6 per cent. at 840° C., i.e. generally about 40° C. above the critical range. Except in the case of steel, heat treatment before, during, or after cold-working is usually carried out to soften the metal fully by annealing. The temperature selected is one at which complete recrystallization will take place in a relatively short time, and it would appear in the first instance that large variations are permissible between a temperature that is too low to soften the metal and one that is so high that excessively large grains are produced. But the temperature at which rapid softening occurs rises as the amount of impurities increases and as the previous amount of cold-working decreases, so that the annealing temperature must be sufficiently high to allow for variations. The crystal size resulting from annealing increases with the temperature and if this is too high the grains may be too large. Thus the permissible range is narrowed down, and furthermore, for certain working operations, notably the production of pressings, the grain size is frequently of critical importance and an exact annealing temperature must be maintained.

In heat-treating operations designed to modify the structure and constitution of alloys by controlling the conditions under which changes take place, the exact temperature is usually very important. In the hardening of carbon steels containing less than 0.9 per cent. of carbon it is necessary that they should be heated above the critical range in order that they may be entirely converted to austenite, but it is also necessary that they should not be heated far above this, otherwise large grains will develop and the tendency to crack during quenching will increase. Thus the best hardening temperatures for these steels are about 15° to 20° C. above the critical range. In hardening carbon steels containing more than 0.9 per cent. of carbon, the object of the heating is to convert all the pearlite to austenite but to leave the carbon in excess of 0.9 per cent. in the form of undissolved cementite. For this purpose the steel is heated to about 760° C. If a lower temperature is used some of the pearlite may not be converted to austenite, and if a higher one, too much cementite will be dissolved and the higher quenching temperature will increase the danger of cracking. In general, for the hardening of each particular type of carbon or alloy steel there is a narrow range of temperature in which it should be heated, and if this is exceeded or not reached the best results will not be obtained. The same applies to tempering, and the subject will be further discussed in Part V. The solution treatment of aluminium alloys must also be conducted within certain narrow temperature limits which vary with the alloy, and this will be further considered in Part VI.

Experienced men can become very expert at judging temperatures from the colour of the stock or the furnace walls, and in the past, estimation of the temperature was entrusted to the furnace operators. For modern purposes, however, the skill of such men is not enough. All tools made from the same steel are now expected to give about the same

performance, forgings of the same steel are expected to machine under the same conditions, consignments of metal of the same type are expected to respond in the same way to hot- and cold-working operations, parts made to the same specification are expected to show the same behaviour in service, and in general every metallic article is expected to behave in a predetermined way during treatment and service. None of these expectations are completely realized, and whenever the manufacturing or service conditions are exacting, rejections and failures are common, but as knowledge accumulates, the possibility of preventing departures from anticipated behaviour increases, and an important step towards this end is to see that heating operations are carried out at the selected temperature. This has led to the almost universal installation of pyrometers, except in small jobbing shops. These are generally of the recording type, so that if they are properly calibrated and kept in order a permanent record is made of the temperature in the furnace. Pyrometers, of course, only register the temperature of the positions where they are located, and their installation does not diminish the importance of designing the furnace, applying the heat, and packing the stock so that the whole charge is heated to the prescribed temperature. They indicate the temperature but they do not control it, and the maintenance of the correct temperature depends on the furnace operators who must adjust the fuelling or the draught to keep the temperature as indicated by the pyrometer within the prescribed limits. With the introduction of the electric furnace, attention was directed to the advantages of automatic furnace control which eliminates the uncertain human element. Such control is most conveniently obtained by means of an electrical thermostat, and its application to an electric furnace is simple. All that is necessary is a relay which is operated by the thermostat and cuts off the current when the temperature rises above a prescribed maximum and makes connexion again when it has fallen to a prescribed minimum. In furnaces fired by gas, oil or coal the installation of temperature control is not so easy. Nevertheless, suitable devices are available, and a thermostatically operated relay is made to control the flow of fuel through suitable valves, and even in ordinary coal-fired furnaces thermostatic control of the mechanical stoker can be arranged.

Although it is never a critical factor, the duration of heating is generally important. Except in a few cases this should at least be such that the metal is heated throughout to the selected temperature. After this, heating may be continued if necessary to permit any required constitutional change to take place. When small articles are being heated individually, the interior reaches the required temperature shortly after the surface, and no special allowance has to be made for mass effect. When, however, small stock is packed in boxes or when large stock is being heated this must be allowed for. The temperature gradient established in a given mass during heating increases with the

rate of heating, and the time required for this to be eliminated after the outside has reached the necessary temperature increases with the steepness of the gradient. Consequently, the length of time that the mass must be maintained at a given temperature after the outside has reached it increases with the rate of heating. In so far as uniform heating is concerned, duration and rate must therefore be considered together, and at the same time account must be taken of available methods of controlling the rate.

The rate and duration of heating assume their greatest importance in the treatment of steel, for large masses of other metals are not often heat treated, and owing to their greater ductility they are in any case less liable to develop internal cracks during too rapid heating. As it is only at lower temperatures that steel is sufficiently rigid to crack under thermal stress, it is the rate of heating up to about 650°C . that is important. During the re-heating of stock at intermediate stages in hot-working, the metal is above this temperature before the re-heating begins, so that it is only during the first re-heating of cold ingots or of forgings that have been allowed to cool that the question of careful heating from a low temperature arises. For this purpose the metal is charged into a furnace maintained at about 500°C . and then heated uniformly to $600\text{--}650^{\circ}\text{C}$. before being raised to the forging temperature. Similar precautions have to be adopted in heating high-speed steel tools for hardening, for although these are of small dimensions compared with forging ingots their great hardness makes them very susceptible to cracking under thermal stress.

The actual rates and durations of heating employed vary with the composition of the steel, the size of the mass, the available plant, and the practice in different works. Furthermore, different methods of stating heating conditions are employed, but to give an idea of the times involved some of these may be mentioned. For heating cold ingots of carbon steel the time to reach 650°C . should be about 30 minutes per inch of section (i.e. 40 in. square 20 hours) and to reach forging heat (about $1,280\text{--}1,320^{\circ}\text{C}$.) 1 hour per inch of section. With this rate of heating it is usually considered sufficient to maintain the ingot at the forging temperature for 15 min. per inch of section. For heating alloy steels slower heating and longer soaking are recommended.

In heating steels for hardening the constitutional changes are completed in about the same time as the metal is uniformly heated so that the recommended practice is similar to the above, i.e. for carbon steels, heat to the requisite temperature at the rate of 1 hour per inch and maintain the temperature for 15 minutes per inch. In the solution treatment of aluminium alloys, however, a considerable time after the temperature is reached must be allowed for the constitutional change to proceed to the required extent. The same applies to heating for carburizing or nitriding where the object is to bring about a change in the surface layers of the steel by the diffusion into it of carbon or nitrogen.

The rate of heating is only important in so far as the slow heating of large stock reduces the time for which it must be maintained at the maximum temperature and decreases the danger of internal cracking. Apart from this the rate of heating receives little attention, and the gradual heating adopted in continuous furnaces is usually employed because it is more economical than to allow the cold metal to heat up while passing through a part of the furnace maintained at the full heat. The rate of cooling is, however, of much wider significance and is varied and controlled in numerous ways. The datum rate of cooling is that obtained by free cooling in air, and the rate at which a given article cools is then determined by its size. Small articles cool more rapidly than large ones, and in all sizes except the smallest the rate varies considerably from the surface to the centre. Slower cooling than this may readily be obtained by using continuous furnace with a cooling region, by packing articles in boxes, by cooling with the furnace, or by transferring to a furnace held at a lower temperature. All these methods of delaying the cooling tend to reduce the differences between small and large articles and between the surfaces and centres of given articles. They are used when the object of the treatment is to eliminate internal stress, when the development of such stress is to be avoided, or when the hardening of an air-hardening steel must be prevented. Frequently, however, more rapid cooling than that obtained by cooling in air is required. This can also be obtained in a number of ways, e.g. by using an air-blast or a water-spray, or by immersing in oil, water, molten salts, or molten metals of low melting-point. When small stock is being handled the rate of cooling can be varied as required by altering the method of cooling. But as all methods of accelerating the cooling increase the effect of mass, in causing differences in the rates at which articles of different size cool, or in producing differences between the surface and the centre, the control over the rate of cooling decreases as the mass of the stock or the desired rate of cooling increases. Accelerated rates of cooling are most frequently required in the treatment of steel, and the difficulty of rapidly cooling large masses and obtaining a uniform rate of cooling throughout the section sets a limit to the extent to which the constitutional changes can be controlled by the rate of cooling. Elements like nickel, chromium, manganese, and molybdenum have the effect, however, of retarding the constitutional changes, and increasing the content of these has a similar effect to increasing the rate of cooling. Thus, as will be shown in Part V, these elements are frequently added to steel to overcome the limitations imposed on the effects obtainable by rapid cooling by the difficulty of obtaining this in stock of appreciable section.

FURNACE ATMOSPHERES

In every heat-treating operation the heated metal is in contact with some kind of gaseous atmosphere with which it may react in a manner

that depends on the metal, the temperature, and the composition of the atmosphere. The natural atmosphere in electric furnaces is air, while that in fuel-fired furnaces consists of the products of combustion of the coal, oil, or gas. In electric furnaces, however, it is comparatively easy to provide many other kinds of atmospheres, in fuel-fired furnaces the atmosphere may be varied by altering the proportions of fuel and air, and in certain types of these furnaces, in which the metal is protected from the products of combustion, artificial atmospheres can be provided.

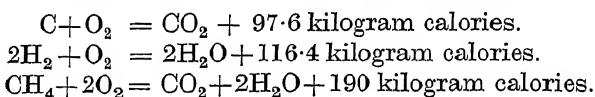
The reactions between the metals and the atmospheres in which they are heated have in recent years been studied from several different points of view. The aspect of primary importance is, of course, the effect of the atmosphere on the metal, and if the performance of a given operation in a particular atmosphere results in difficulties in subsequent treatment or unsatisfactory behaviour in service, the desirability of changing the atmosphere is indicated. From this arises the need for studying the effects on metals of a variety of different atmospheres so that inert or substantially inert atmospheres may be discovered. When these have been found the problems of producing the desired atmospheres and designing furnaces in which they can be maintained have to be dealt with, and finally, when the technical factors have been fully considered, it remains to balance the anticipated advantages of inert atmospheres against the costs of installing the necessary plant and providing the selected atmosphere.

Natural furnace atmospheres, i.e. air or the products of the efficient combustion of fuel, have an oxidizing effect on metals generally and certain types of atmosphere have the effect of decarburizing steel. From the point of view of subsequent treatment or behaviour in service these effects are frequently undesirable. They may be wholly or partly prevented by reducing the air supply in fuel-fired furnaces or by providing artificial atmospheres in electric and certain types of fuel-fired furnaces. This, however, increases the cost of the treatment, and the advantages of decreasing or eliminating oxidation or decarburization have to be considered in relation to the expense of reducing thermal efficiency or providing plant and materials for maintaining artificial atmospheres. When atmospheres other than air or those arising from the efficient combustion of fuel are used in order to decrease scaling they are described as controlled atmospheres, and although such control has long been used to a certain extent its wide application is comparatively recent. This has been promoted by a number of factors among which may be mentioned (1) the accumulation of knowledge on the undesirable effects of scaling and decarburization, (2) the increased use of metals under conditions in which the efficiency is influenced by scaling or decarburization, (3) the increased use of electric furnaces in which atmosphere control is simplified, and (4) the accumulation of knowledge on inert or substantially inert atmospheres and methods of producing them. The purpose of this section is to consider natural furnace

atmospheres, their effects on metals, and methods of atmosphere control which diminish or eliminate these effects.

Natural Furnace Atmospheres.

The natural atmosphere in electric furnaces is air which consists of oxygen and nitrogen. The natural atmosphere in fuel-fired furnaces consists of nitrogen plus the products of chemical reactions between the oxidizable constituents in the fuel and the oxygen in the air. The principal constituents of primary fuels such as coal, oil, and natural gas are carbon and hydrogen and compounds of these elements known as hydrocarbons. Under the appropriate conditions these substances combine with oxygen according to the following equations:



Certain quantities of heat, measured in kilogram calories, are liberated and the products of combustion are carbon dioxide and water vapour. Gaseous fuels contain carbon monoxide instead of carbon, but in combustion this is also oxidized to carbon dioxide.

If the operation of a fuel-fired furnace could be arranged so that the fuel was completely burned with the theoretical amount of air, then the furnace atmosphere would consist of nitrogen, carbon dioxide, and water vapour. If, however, there is a deficiency of air and complete combustion does not occur, then the atmosphere will also contain carbon monoxide (resulting from partial oxidation of the carbon), hydrogen, and unburnt hydrocarbons (e.g. CH_4), and when the supply of air is very deficient particles of solid carbon may be carried by the gas stream. When, on the other hand, there is an excess of air, carbon monoxide, hydrogen, and unburnt hydrocarbons are absent from the furnace atmosphere which contains oxygen in addition to carbon dioxide, nitrogen, and water vapour.

It follows from the above that the natural atmospheres in furnaces mainly consist of different mixtures of nitrogen, oxygen, hydrogen, hydrocarbons, carbon monoxide, carbon dioxide, and water vapour plus small amounts of other gases of which the most important are sulphur compounds. Of these gases, nitrogen is inert, oxygen, carbon dioxide, water vapour, and sulphur dioxide are oxidizing, while hydrogen, carbon monoxide, and hydrocarbons are reducing. Where steel is concerned, however, carburizing and decarburizing have also to be considered, and in this connexion hydrogen, oxygen, and carbon dioxide are decarburizing, carbon monoxide and hydrocarbons are carburizing, while water vapour greatly accelerates the decarburizing effect of hydrogen.

In order to utilize completely the heating value of the fuel burned in a furnace all the carbon should be oxidized to carbon dioxide and all

the hydrogen to water vapour. Knowing the composition of the fuel the theoretical amount of air required can be calculated from the chemical equations. In practice, however, excess air must be provided to ensure complete combustion, and the amount depends on the intimacy of contact or mixture between the fuel and the air. In gas-fired furnaces intimate mixture of the air and gas is comparatively easy to arrange, and only a small excess of air is necessary. With oil fuel a greater excess is required, and the complete combustion of coal requires from 50 to 100 per cent. excess air.

An atmosphere resulting from complete combustion with the requisite amount of air is frequently described as 'neutral', while those containing free oxygen on the one hand or carbon monoxide, hydrogen, and hydrocarbons on the other are described as 'oxidizing' and 'reducing' respectively. These terms, however, do not properly describe the action of the atmospheres concerned on metals heated in them, for the carbon dioxide and water vapour present in the so-called 'neutral' atmosphere are capable of oxidizing steel, and an atmosphere must be well in the 'reducing' range before it is really 'neutral'. In fact the term neutral is one that can hardly be used in a general way in connexion with the relations between metals and atmospheres, for an atmosphere that may not oxidize steel can still decarburize it, and when the concentrations of carbon monoxide and hydrocarbons are increased to such an extent as to prevent this carburization is liable to occur.

In general, air and the atmospheres resulting from efficient combustion of fuel are capable of oxidizing metals at rates that increase with temperature. If this oxidation is to be prevented, the air in electric furnaces must be replaced by some other atmosphere, and in fuel-fired furnaces the supply of air must be cut down so as to result in an atmosphere containing fairly high proportions of hydrogen, carbon monoxide, and hydrocarbons. If this is done, however, thermal efficiency is sacrificed, and it may not then be possible to attain the required temperature. Furthermore, if the metal concerned is steel, prevention of oxidation is not the only factor, for decarburization and carburization have also to be considered. In the following discussion of the effects of oxidation, &c., and atmosphere control, steel and non-ferrous metals are dealt with separately because of the conspicuous differences between them.

SCALING, BURNING, AND DECARBURIZATION OF STEEL

Scaling.

The mechanism of scaling and the factors that produce it are considered in Chapter VIII where it is shown (1) that heated steel is oxidized by oxygen, carbon dioxide, and water vapour, and a wide range of gas mixtures containing these, and (2) that the rate of scaling increases with temperature and is further increased by the presence of sulphur dioxide in the atmosphere. Methods of preventing scaling in

service are considered in Parts V and VI, and in this chapter attention will be confined to the effects of scaling during heat treatment and hot-working and the methods of preventing it.

One of the most obvious effects of scaling is that a certain amount of metal is converted to oxide and thus wasted, but at the present time preventive measures are not adopted simply to eliminate waste. The highest temperatures and longest times of heating are used during heating for hot-working, and it is in such operations that the greatest amount of metal is lost, but in considering the importance of this a number of factors must be taken into account. It is seldom possible to produce ingots free from surface defects, and scaling during the heating of these provides an alternative to machining as a means of improving the surface. This is an advantage of scaling of which wide use is made. To secure it, however, the scale must flake off readily during working, for otherwise it will be rolled or hammered into the metal and cause surface defects and difficulties in machining besides damaging rolls and forging dies by abrasive action. Any attempt to decrease oxidation, short of preventing it altogether, results in a tenacious in place of a loosely adhering scale, and as the metal will scale during working in any case, there does not appear to be much advantage in going to the expense of heating in an inert atmosphere. Thus during heating for working, free scaling is permitted, and loss of metal is accepted in order to improve the surface of the ingot and avoid as far as possible the effects of adherent scale.

The formation of scale when the metal is being heated before cold-working is quite a different matter, for it must be removed by pickling or abrasive blasting before the working operation. As fabrication by cold-working frequently involves a number of intermediate heatings, each must be followed by pickling unless scaling during heating is prevented. It is in this connexion therefore that control of the furnace atmosphere is most frequently employed. Furthermore, scaling during these operations, and when the metal is being annealed after cold-working, tends to impair its surface, and in order to improve the surfaces obtained on cold-worked products, to facilitate polishing, or to secure good coatings of tin or zinc, heat treating in controlled atmospheres is employed.

Scaling during heating for hardening has several pronounced disadvantages. When this operation has to be performed it is necessary to machine to near the finished dimensions before hardening. Any scaling that takes place subsequently, leads to a change in dimensions. It is possible to control the furnace atmosphere so that a given amount of scaling will occur, and to allow for this in machining, but as slight fluctuations in the atmosphere are liable to lead to undersized parts that must be rejected or to oversized parts that must be ground to size, it is usually desirable to heat articles like fine tools and gauges, &c., under non-oxidizing conditions. Furthermore, the presence of oxide on

the surface of articles that have to be quenched in water, oil, salt, or molten metal may seriously retard the cooling. From this point of view thin scales are a greater disadvantage than thick ones, for they adhere more tenaciously and do not split off so readily on immersion. Scale is more likely to interfere with cooling when the quenching medium is oil than when it is water, for the more drastic chilling in the latter medium splits it off more effectively. Frequently, although most of the scale flakes off on immersion small pieces remain clinging to the part, and as the metal under these is not properly quenched 'soft spots' are the result.

In the treatment of steel the prevention of oxidation or the removal of scale is only resorted to in connexion with cold-working, hardening, surface finishing or surface coating. During hot-working and the heat treatments that accompany it, scale is formed, and a large amount of steel goes into service with this adhering either wholly or partly to the surface. It has been shown that whether the metal is painted or not this scale tends to promote corrosion. If the coating is complete, corrosion is less rapid than when it is discontinuous, but the resistance to corrosion is greatest when all scale is removed.

Burning.

'Burning' is not entirely due to the nature of the furnace atmosphere nor is it confined to steel, but it is affected by the furnace atmosphere and is most important in connexion with the heating of steel for hot-working and may therefore be considered here. The term is used to describe a phenomenon that is associated with heating at too high a temperature and consists of intercrystalline weakness. If the burning is severe, the metal may fracture during working, but if it is not, and the method of working is not drastic, the burnt metal may pass into service and subsequently fail by intercrystalline rupture. Three aspects of the phenomenon may be distinguished, namely, the conditions under which it occurs, the mechanism on which it depends, and the effects to which it gives rise. In connexion with the last of these all that need be said is that the intercrystalline cohesion is weakened and the metal becomes liable to fail during working or in service. The other aspects can be discussed together because of their close relations.

It may be said in the first place that many factors come into play in burning, and the exact way in which they combine in a given case is difficult to discover. Under certain conditions burning may consist of the formation of voids between the crystals, under others it may consist of the formation of voids and the subsequent oxidation of their surface, while under others it may consist of the formation of oxide films between the crystals without the previous appearance of voids. It is well known that the cohesion between the crystals in a metal decreases rapidly before it is destroyed altogether when actual melting begins. In a range of temperature close to the melting-point it is therefore to be expected that failure of intercrystalline cohesion will occur readily.

The force of surface tension which tends to make each crystal assume as nearly as possible a spherical shape may be sufficient under certain conditions to destroy the cohesion between them. In general, however, owing to the temperature gradients established during heating some internal stress will exist in the metal, and as this results in tension in the interior it may cause intercrystalline rupture there when a sufficiently high temperature is reached. In addition to these factors the effect of gas must also be considered. When copper containing oxide is heated in an atmosphere containing hydrogen this gas penetrates the metal, reacts with the oxide and forms water vapour, which being unable to diffuse away builds up a pressure at the crystal boundaries and forces the crystals apart. A similar effect might be produced in steel by the formation of carbon monoxide in a reaction between carbon and oxygen absorbed from the atmosphere. Should these factors alone or in combination be incapable of producing intercrystalline voids while the metal is heating, they may nevertheless weaken the cohesion to such an extent that such voids are formed during working. In this case, if the outside of the ingot or billet is considerably hotter than the interior, the voids will be formed near the surface, whereas if the whole is at a uniform temperature the voids are most likely to occur in the interior which has less chance to cool in the interval between withdrawal from the furnace and the commencement of working.

From the point of view of burning, the melting temperature of the steel is not that obtained from the iron-carbon diagram. The solidus line in this diagram represents the temperatures at which solidification is completed in small crucibles containing the steel. During continuous heating melting will not begin until the solidus is passed, but when the metal is maintained at a constant temperature melting may begin at the solidus. In any case this line applies to the beginning of melting in homogeneous iron-carbon alloys. The presence of manganese, silicon, and phosphorus will lower the temperature at which it begins even if they are uniformly distributed. In steel ingots and billets, however, the impurities carbon, silicon, manganese, and phosphorus are not uniformly distributed but are more highly concentrated at the boundaries of the original crystals than elsewhere. The melting-point in these regions may therefore be considerably below the solidus or the melting-point of the steel generally. This gives rise to the idea of incipient melting, i.e. fusion of the metal in regions where impurities are concentrated. Burning has frequently been attributed to this phenomenon, and it is undoubtedly one of the factors involved, but it does not account for all its aspects such as the fact that burning may be produced in the interior of a mass while the outside remains sound. Clearly, incipient melting can explain the formation of intercrystalline voids near the surface, but it is not so easy to apply it to the interior, for a void is not formed unless the fused metal can flow away. The extent to which incipient melting alone is responsible for intercrystalline voids is

uncertain, but it is clear that as it is the melting-point of the intercrystalline metal that is concerned in connexion with the effects of surface tension, internal stress, and liberated gas discussed above, the fact that this is lower than that of the metal generally has an important bearing on the effect of these phenomena.

It was shown in Chapter VIII that when steel is exposed to an oxidizing atmosphere, oxygen may penetrate the metal and form films at the crystal boundaries. This will result in intercrystalline weakness and therefore is a factor in burning. If the metal is sound the formation of these oxide films should begin at the surface and proceed inwards, but if voids have already been formed the oxygen will tend to proceed along them and form oxide films in them. It is also possible that if voids are formed in the interior while the outside remains sound oxygen may diffuse through the sound metal and form oxide in the voids.

Jominy (272) has shown that steel may be burned by heating in a vacuum. Clearly, therefore, oxygen or other gases are not essential factors. Burning *in vacuo* is evidently due to some kind of combination of weakening of cohesion, surface tension, internal stress, liberation of dissolved gas or gas produced by a reaction, and incipient fusion, but other factors become effective when a gaseous atmosphere is present. Thus the same author has also shown that while steel burns in neutral or reducing atmospheres when heated near the solidus it burns at temperatures 100° C. below the solidus when the atmosphere is oxidizing. Small specimens were used in the experiments and as heat is liberated in the oxidation of iron, this might have raised the temperature of the metal heated in an oxidizing atmosphere above that of the furnace. In some of the experiments, however, the thermocouple was near enough to the metal to give its temperature rather than that of the furnace, and it appears therefore that the presence of oxygen actually lowers the burning temperature. This is recognized in practice and strongly oxidizing atmospheres are regarded as being dangerous from the point of view of burning. To some extent this will be due to the formation of intercrystalline films of oxide, but it may also be due to the production of carbon monoxide within the metal by reaction between oxygen and carbon.

Decarburization.

Decarburization, i.e. the removal of carbon from the surface of steel during heat treatment or hot-working, is a phenomenon that sometimes has serious consequences. If the product is machined after all heating operations are completed, as is the case with many articles, the decarburized layer is removed and is therefore of no consequence, but if the metal goes into service without machining or is heat treated after machining, the decarburized layer remains. Tools and other articles that have to be hardened are machined as near the finished size as possible before final heat treatment. If decarburization occurs

during this treatment the surface will not harden properly, and a soft skin, which is very undesirable in tools or parts subjected to wear, results. Such treatments should therefore be performed in atmospheres that do not decarburize. Large amounts of steel go into use, however, without being machined at any stage, and the decarburization that takes place during all the heating operations affects the surface of the product. Until quite recently, the presence of such a surface on steel articles other than tools, gears, and parts subjected to wear and abrasion was not considered a serious disadvantage, but as explained in Chapter VII it is now known that decarburization seriously reduces the endurance of parts subjected to repeated stress.

The decarburization of mild steel is not in general a serious matter. Such steel is mainly employed where ductility rather than strength, hardness, or resistance to repeated stress is required, and surface decarburization does not impair ductility. Furthermore, the amount of carbon removed under given conditions of time, temperature, and atmosphere decreases with the carbon content, so that the effect of given conditions on mild steel is less than on steel of higher carbon content. Finally, as the carbon content of the surface layer can only be reduced to zero, the difference in properties between the decarburized surface and the remainder of the material will tend to decrease with the original carbon content and reach a minimum in low carbon steels. When, however, mild-steel sheets have to be subjected to deep-drawing operations, such as are involved in the manufacture of motor-car bodies, decarburization is a serious defect because it promotes the development of 'stretcher strains' which are the result of unequal stretching of the sheet. Although all the decarburization that occurs from the first heating of the ingot onwards may be supposed to affect this, it is only that which occurs during the annealing or normalizing of the sheets before, or at intermediate stages in working, that is of marked importance. The reason for this is that decarburized layers produced during the early stages of heating are small in proportion to the section of the material and are rolled out with it until their depth is practically negligible, whereas those produced during heating of the sheets are of substantial depth in relation to the thickness of the sheets. Thus it is at this stage that the advantages of heating in controlled atmospheres are important.

The furnace gases that can produce decarburization are hydrogen, water vapour, carbon dioxide, and oxygen, but as the last three also produce scaling, they can only be regarded as effective in decarburizing when the conditions are such that decarburization is more rapid than scaling i.e. when a decarburized layer is formed under the scale layer. Such conditions depend on temperature and pressure, and in the general case of mixed gases, on the relative proportions of the different gases present. This will be discussed presently, meanwhile the mechanism may be considered. The most commonly accepted view is that the

decarburizing gas (e.g. hydrogen) diffuses into the metal, combines with carbon, and removes it as a compound gas (e.g. CH_4). There is no evidence, however, for assuming the inward diffusion of hydrogen and the outward diffusion of methane, and it is much more probable that the reaction between carbon and hydrogen takes place at the surface of the metal to which carbon from the interior diffuses to replace that which is lost. The same process occurs when other decarburizing gases are concerned.

Decarburization results in the removal of a certain amount of carbon from the steel, but as the removal takes place at the surface it does not result in a gradual diminution of the carbon content of the metal as a whole. What really occurs is that the carbon content of the surface is reduced to a low value and carbon from the interior diffuses outwards thus establishing a carbon concentration gradient. In considering decarburization it is therefore necessary to take account of the total amount of carbon removed and the carbon gradient established during this removal.

We may deal in the first place with the conditions that arise when a steel is decarburized at a temperature above 906°C . (i.e. the temperature of the polymorphic change in iron). At the beginning, the steel consists of a uniform solution of carbon in γ -iron and no matter how much carbon is removed there is no formation of α -iron. In the removal of carbon from such a steel two factors are involved: (1) the rate at which it is converted to CH_4 or other volatile compound at the surface, and (2) the rate at which it diffuses from the interior to the surface. This second factor depends on the combination of two others: (a) the rate at which carbon can diffuse from a region of high concentration to one of low concentration, and (b) the difference in concentration between the regions of high and low concentration respectively. The factors that ultimately affect the process are (1), (a), and (b) and any of these may be the controlling factor, i.e. the factor that compels the slowest rate of removal of carbon. The carbon gradient established after a given time under given conditions will vary according to the relations between the three factors.

Factor (1) depends on the temperature, pressure, and composition of the atmosphere, factor (a) on the temperature of the metal, and factor (b) on the difference in carbon content between the surface and interior of the steel. The rate of removal of carbon will clearly tend to increase with increase in the rate of the surface reaction (1), increase in the temperature (a), and increase in the carbon content of the steel (b). This result will obviously be obtained when all three are increased together, but owing to the mutual relations of the factors it will also be obtained when one is increased while the others are maintained constant. Thus if a high carbon steel is substituted for a low carbon steel while the other conditions remain the same, more carbon will be removed per unit of time because more will reach the surface and there increase the concentration of carbon with which the atmosphere may react.

The effect of the relations between the factors considered above on the carbon concentration gradient is rather more complicated. If factor (a) and the carbon content are kept constant, the carbon gradient will become steeper as the rate of reaction at the surface is increased by changing the atmosphere. The same result will be obtained if the carbon content is increased while the other conditions remain constant, but if the atmosphere and carbon content are kept constant while the temperature is raised, the effect on the gradient will depend on whether the rate of reaction at the surface (1), or the rate of diffusion in the steel

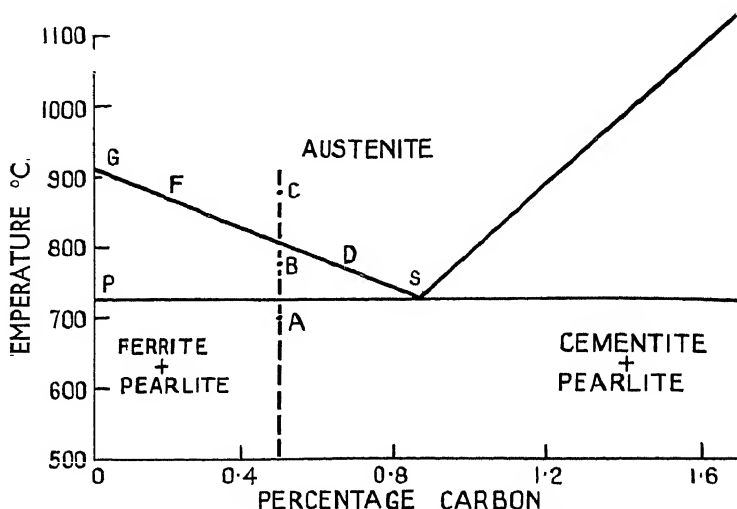


FIG. 239. Steel portion of the iron-carbon diagram.

(a) increases most rapidly with temperature. If (1) increases more rapidly the gradient will become steeper, whereas if (a) increases more rapidly the gradient will become shallower. In any case, the carbon gradient after the steel is cooled is influenced by the fact that it passes through the critical range during cooling, as explained below.

Decarburization in Relation to the Iron-Carbon Diagram.

The above discussion of the process of decarburization applies to the conditions realized when the iron remains in the γ -form throughout. Other factors are introduced, however, when decarburization takes place (1) below the lower limit of the critical range (line PS , Fig. 239), (2) between the upper and lower limit of the critical range (lines GS and PS), or (3) above the upper limit of the critical range of the steel but below the temperature of the polymorphic change in carbonless iron (G). Furthermore, when decarburization occurs within or above the critical range, the fact that the steel is subsequently cooled through this range has an influence on the final distribution of carbon.

If a steel containing 0.5 per cent. of carbon is considered, the three

conditions mentioned above are obtained by decarburizing at points *A*, *B*, and *C* respectively (Fig. 239). When heated to point *A* the steel consists of ferrite, which contains less than 0.035 per cent. of carbon in solution, and pearlite which contains 0.9 per cent. of carbon in the form of plates of Fe_3C interlaminated with plates of ferrite (Figs. 162, 163, Chapter VI). The general arrangement of the ferrite and pearlite will vary according to the previous treatment of the steel (Chapter XI), but considering the free ferrite and the ferrite in the pearlite together, it may be said that the plates of Fe_3C are isolated from each other and surrounded by ferrite. Except for such plates of Fe_3C as are exposed at the surface when decarburization begins and are soon decarburized, the removal of carbon involves diffusion from the plates of Fe_3C through ferrite to the surface of the steel. As the diffusion of carbon in ferrite is slow, decarburization is also slow.

Soon after decarburization begins the carbon content at the surface will be reduced to zero and a thin layer of carbonless ferrite will be formed. Some distance below the surface the ferrite will be saturated with carbon (i.e. contain about 0.03 per cent.) and between the carbonless and the saturated regions a concentration gradient will exist. It is this gradient and the rate of diffusion of carbon in ferrite that are concerned in the migration of carbon to the surface. The function of the Fe_3C is simply to keep the ferrite in contact with it saturated with carbon. Plates of Fe_3C below the surface are not affected until the carbon content of the ferrite in contact with them falls below the saturation value, i.e. until it comes into the region of the concentration gradient. When this occurs these plates begin to supply carbon to the ferrite. At any stage therefore the concentration gradient extends from the surface to the nearest Fe_3C .

In general, therefore, the first stage in decarburization is the formation of a minute carbonless layer on the surface. Close to this the carbon content of the ferrite is maintained at saturation by carbon coming from Fe_3C , and between the carbonless and saturated ferrite there is a concentration gradient. As the Fe_3C nearest the surface is decarburized, the inner limit of the gradient moves towards the interior and two zones are established in the steel: (1) the outer, which consists entirely of ferrite in which the carbon content varies from 0.03 per cent. to zero, and (2) the inner, which consists of ferrite and pearlite and contains on the average 0.5 per cent. of carbon. From the outer surface of this inner zone carbon is supplied to the outer zone, but there is no migration of carbon within the inner zone, and decarburization proceeds mainly by the extension of the outer zone towards the interior. The general result is that the steel consists at all times of a layer of practically carbonless ferrite surrounding a core that is practically unaltered, and the conditions are quite different from those previously shown to apply to decarburization above 906°C .

If decarburization is performed at the temperature of point *B* (Fig. 239)

the conditions are somewhat similar to those just described. When first heated to *B* the steel consists of ferrite containing very little carbon, and austenite containing the amount represented by point *D*. The austenite occupies more volume than that occupied by the pearlite at point *A*, but the relative distribution of the ferrite and austenite depends on the previous treatment of the steel and its carbon content as described in Chapter XI. In general, therefore, in dealing with steels heated in the area *GSP* it is difficult to say to what extent the austenite is continuous and to what extent it exists in isolated regions surrounded by ferrite. In any case, so long as both phases are present, the result appears to be about the same. At the beginning of decarburization nearly all the carbon is removed from the surface which thus becomes a layer of ferrite. Diffusion through this layer is controlled by the difference in carbon content between its outer and inner surfaces, and the inner surface is maintained at saturation value by carbon from the austenite. As the carbon is removed from the austenite it changes to ferrite and in this way the outer zone of ferrite increases in depth. Thus the process of decarburization resembles that described above. The function of the austenite is to keep the ferrite in its vicinity saturated, and as the austenite is of composition *D* and cannot lose carbon without changing to ferrite it is converted progressively to ferrite as decarburization proceeds. At all times during the process the steel will therefore consist of an outer zone of ferrite containing practically no carbon and a core of austenite and ferrite of the same average composition as the original steel.

Somewhat different conditions are realized when decarburization occurs at the temperature of point *C*. On reaching this temperature the steel is a uniform solid solution of this composition. Removal of carbon from the surface then begins. So long as the carbon content at the surface remains greater than that represented by point *F*, the surface remains austenite and the conditions are similar to those first considered. Continued removal of carbon, however, converts the surface to a mixture of austenite and ferrite and finally to ferrite. Thus, as in previous cases, an outer layer of ferrite is formed, removal of carbon depends on diffusion through this layer, and the function of the remaining austenite is to keep the inner surface of the ferrite zone supplied with carbon. There is an important difference between this case, however, and that just considered, in that the core of austenite is continuous and its average carbon content is considerably higher than is required to prevent it from changing to ferrite. When, therefore, the austenite in contact with ferrite supplies carbon to this ferrite it may remain austenite and the carbon lost may be replaced by diffusion from the austenite nearer the interior.

At the time when the outer layer of ferrite is first formed the austenite in immediate contact with it will be of composition *F*. Thereafter, as decarburization proceeds carbon is supplied to the outer ferrite zone

from the austenite of composition F and this tends to cause it to transform to ferrite. At the same time, however, carbon diffuses from the austenite in the interior to that at the ferrite-austenite interface, and tends to keep it at composition F and therefore austenitic. In so far as carbon is removed from the austenite in contact with ferrite more rapidly than it is supplied from the interior, decarburization proceeds by the advance of the ferrite zone. But, in so far as carbon is supplied from the interior to the austenite in contact with ferrite as rapidly as it is removed, decarburization tends to proceed by the gradual diminution of the carbon content of the austenite. The relations between these two processes, i.e. advance of the ferrite zone and diminution of the carbon content of the austenite generally are capable of many variations. Of these only the effect of temperature need be considered here.

The range of temperature under consideration extends from that at which the line representing the composition of the steel meets the line GS (Fig. 239) to the highest temperature at which ferrite can exist, i.e. 906°C . (point G). As the decarburizing temperature is raised from the lower to the upper limit of this range, the rate of diffusion of carbon in ferrite and austenite increases. Unless there is a pronounced difference in the rate of this increase in ferrite and austenite respectively, it will not affect the relations between the two processes mentioned above. At the same time, however, the saturation concentration of carbon in ferrite decreases as the temperature is raised and this will tend to reduce the amount of carbon diffusion through the ferrite. Furthermore, as the temperature is raised the carbon content of the austenite in contact with ferrite decreases as shown by the line SG , but the carbon content of the austenite remote from ferrite remains the same. This has the effect of increasing the concentration gradient in the austenite and promoting the diffusion of carbon towards the austenite-ferrite interface. Thus raising the temperature promotes diffusion from the interior to the austenite-ferrite interface more than it promotes diffusion from this interface towards the surface of the steel. Consequently, as the temperature is raised, decarburization takes place to a greater extent by the gradual diminution of the carbon content of the austenite and to a lesser extent by the advance of the ferrite zone. Thus as the temperature is raised from the upper limit of the critical range to the temperature of the polymorphic change in iron, the process of decarburization changes gradually from that characteristic of temperatures within and below the critical range to that characteristic of temperatures above that of the $\gamma \rightarrow \alpha$ change in iron.

Summarizing the relations between the process of decarburization and the iron-carbon diagram it may be said, that when it occurs below the line PS or in the area GSP it proceeds by the increase in depth of an outer zone of ferrite, while the metal below the zone remains substantially unaltered. Consequently, there is a sharp line of demarcation

between the decarburized and unaffected regions. When it occurs above the temperature of point G , however, no ferrite zone can form, and decarburization leads to the establishment of a carbon concentration gradient. Thus the carbon content rises gradually from the surface and reaches that of the original steel at some distance below it. In the range of temperature between line GS and point G both of the above processes occur, i.e. decarburization takes place partly by the advance of a ferrite zone and partly by the establishment of a concentration gradient in the austenite. As the rate of decarburization tends in general to increase with the temperature, the depth of the ferrite zone formed under given conditions increases as the temperature is raised from any temperature below the critical range to the upper limit of the critical range. Above this the depth of the ferrite zone begins to decrease and becomes zero at the temperature of point G . In this range, however, the rate of decarburization continues to increase but it is accompanied by the withdrawal of greater amounts of carbon from the remaining austenite. Above point G no ferrite zone is formed and raising the temperature is accompanied by the establishment of more pronounced gradients in the austenite.

When a steel that has been decarburized above the temperature of point G is cooled, it passes through the critical range, and the formation of ferrite begins at the surface where nearly all the carbon has been removed. As the temperature falls, the formation of ferrite proceeds from the surface towards the interior into regions of progressively increasing carbon content, and the carbon from these regions is driven in front of the advancing ferrite. This continues through the region of the concentration gradient until a point is reached at which the diffusion of carbon away from the ferrite and diffusion of carbon within the austenite have brought all the remaining austenite to a uniform carbon content. The formation of ferrite then begins at austenite grain boundaries throughout the metal and thereafter the conditions are the same as if no decarburization has occurred. Thus although no outer carbonless zone is formed during decarburization above the temperature of point G , the conditions that arise during cooling tend to produce such a zone, and to result in a sharp line of demarcation between a carbonless outer region and a core in which the carbon is uniformly distributed. This effect of cooling becomes more marked as the rate of cooling is decreased so that the final distribution of carbon observed microscopically, or determined by chemical analyses of successive layers, depends on the relations between the rate of cooling and the concentration gradient previously established as well as on the other factors already mentioned. The conditions realized during subsequent cooling also tend to increase the depth of the ferrite zone in specimens decarburized between the line GS and the temperature of the point G .

Decarburization is due to a reaction between hydrogen and carbon leading to the formation of methane, to reactions between oxygen or

carbon dioxide and carbon leading to the formation of carbon monoxide, or to reaction between water vapour and carbon leading to the formation of methane and carbon monoxide. These reactions may, however, also proceed in the reverse direction, i.e. carbon monoxide or methane may be dissociated at the surface of the steel and the carbon thus produced may diffuse into it. This is the phenomenon of carburization which is discussed in Chapter XIII. Full consideration of the phenomena of carburization and decarburization involves in the first place study of the relations between various pairs of gases and steels of different carbon content under different conditions of temperature, pressure, and gas concentration. Thus mixtures of carbon monoxide and carbon dioxide may either carburize or decarburize steel according to the proportions of the gases present, the carbon content of the steel, the temperature, and the pressure. The same applies to mixtures of hydrogen and methane, oxygen and carbon monoxide, &c. For each system a gas mixture that is in equilibrium with steel of a given carbon content at a given temperature and pressure may be discovered, and such a mixture will neither carburize nor decarburize under these conditions. In practice, however, it is impossible to maintain equilibrium conditions, and consequently either slight decarburization or slight carburization has to be permitted. Furthermore, when the atmosphere contains more than two gases, equilibrium conditions are more difficult to determine and to maintain, and this is the situation that arises in practice. Finally, the decarburizing gases, oxygen, carbon dioxide, and water vapour are also capable of oxidizing steel, while the decarburizing gas, hydrogen, and the carburizing gases carbon monoxide and methane are reducing. As in practice, oxidation, decarburization, and carburization have generally to be considered together, the oxidizing and reducing effects of the gases must also be taken into account.

It will be shown in the next section that atmospheres may be carburizing and reducing, decarburizing and reducing, or decarburizing and oxidizing. In this last case decarburization tends to remove the carbon from the surface layer of the steel while oxidation tends to convert the whole layer to oxide. Whether the steel will finally have a decarburized surface or not depends therefore on which of these processes goes on most rapidly. If the carbon is removed from the surface more quickly than the iron is oxidized, there will be a decarburized layer. If, however, the relations are reversed, there will be none.

ATMOSPHERE CONTROL IN THE HEAT TREATMENT OF STEEL

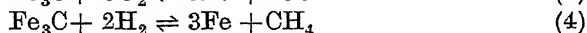
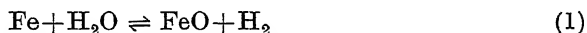
Four general methods are available for controlling the atmosphere in which steel is heated. Firstly, in furnaces in which the products of combustion come in contact with the metal it may be controlled by adjusting the fuel-air ratio. Secondly, in furnaces of this same type the atmosphere in contact with the metal may be controlled by packing

the metal in boxes in which an atmosphere different from that in the furnace is maintained. Thirdly, in electric furnaces and certain types of gas furnaces, in which the fuel burns inside metal tubes (radiant tube furnace) or outside a muffle chamber containing the metal (muffle furnaces) an artificial atmosphere may be provided. Finally, the metal may be heated by immersion in molten salts maintained at the required temperature.

In every heating operation to which steel is subjected some kind of atmosphere control is desirable in the sense that the direct impingement on the metal of a highly oxidizing flame should be avoided, but the extent to which it is necessary, economical, or possible to restrict or eliminate oxidation or decarburization varies from operation to operation. In dealing with the effects of scaling it was pointed out that free scaling during the first heating of ingots has the advantage of improving their surface, and if oxidation is restricted to too great an extent a tenacious thin scale which gives rise to subsequent difficulties is formed. Unless scaling can be prevented altogether there is therefore no purpose in restricting it too much, and as scaling will occur in any case during hot-working there does not appear to be any object in endeavouring to prevent it altogether. Furthermore, important technical difficulties will have to be overcome before it is convenient to heat masses of steel without scaling to the temperature used in heating for hot-working, and even if this were possible it is doubtful whether the advantages gained would compensate for the expense involved. What applies to the heating of ingots also applies to the heating of slabs, billets, and articles forged or rolled from them, so that, in general, in heating steel for hot-working, atmosphere control is not resorted to except in so far as the composition of the products of combustion may be adjusted by reducing the air supply to an extent that does not prevent the desired temperature being attained. As the manufacturing operations progress from the first heating of the ingot to the final heating operation, the advantages of atmosphere control become increasingly greater, and thus it is in connexion with hardening and heating for cold-working that the most rigorous control is employed. The advantages obtainable by the prevention of scaling and decarburization in these operations have already been described, but in some cases there are certain advantages associated with some scaling and decarburization. On stampings required for electrical apparatus a thin evenly distributed oxide film is desirable as it serves as an insulation which prevents the circulation of eddy currents. In other cases a uniform blue scale is desired to provide resistance to corrosion. Furthermore, in the manufacture of wire and pressings, the surface resulting from scaling followed by pickling is supposed to hold the lubricant better than one that has not been scaled during the preceding heat treatment. It appears, however, that in the manufacture of pressings the difficulty can be overcome by selecting the correct lubricant and modifying the die design. In the manufacture

of wire, however, this does not seem to be possible, and unless the wire is provided with a lead or copper coat before drawing, annealing in an atmosphere that produces no scale is not an unmitigated advantage. Finally, in the drawing of high-carbon steel wire a slightly decarburized surface is also an advantage because the thin coating of ferrite acts similarly to copper and lead in preventing seizing.

Of the gases present in air and combustion atmospheres, nitrogen is inert and the others may be classified as oxidizing, reducing, carburizing, or decarburizing. The first stage in atmosphere control is to eliminate free oxygen, for when this is present scaling is very rapid and the danger of burning is increased. Thus as stated in Chapter VIII one experimenter found that varying a combustion atmosphere from 1 per cent. of free carbon monoxide to 1 per cent. of free oxygen was accompanied by a great increase in the rate of scaling, doubling or trebling the metal lost. This has been confirmed by several investigators and is supported by practice, so that unless free scaling is desired the air supply must be adjusted so as to eliminate free oxygen. When this is done six other reactive gases remain, namely carbon monoxide, carbon dioxide, hydrogen, water vapour, methane, and sulphur dioxide. This last gas has a pronounced effect in increasing the rate of oxidation as explained in Chapter VIII, and further experiments on its effects have recently been reported by Preece, Richardson, and Cobb (273). The other five gases are related in pairs to iron, iron oxide, and carbon as follows:



Each of these reactions is reversible, and the direction in which it proceeds depends on the relative concentrations of the gases on the different sides of the equation. Thus, if a mixture of hydrogen and water vapour is in contact with iron and iron oxide the ratio of the concentrations of these gases determines whether iron is oxidized or oxide is reduced. Similarly, if a mixture of carbon monoxide and carbon dioxide is in contact with iron and iron oxide the ratio of the concentrations of the gases determines whether oxidation or reduction occurs. In the same way the ratios $\text{CO}_2 : \text{CO}$ and $\text{CH}_4 : \text{H}_2$ determine whether atmospheres are carburizing or decarburizing.

The first stage in atmosphere control is the elimination of free oxygen, the second is the reduction of the content of sulphur dioxide as far as possible, and the third is the control of the ratios $\text{CO}_2 : \text{CO}$, $\text{H}_2\text{O} : \text{H}_2$, and $\text{CH}_4 : \text{H}_2$. If a mixture of carbon dioxide and carbon monoxide is in contact with oxidized steel at a given temperature and pressure, the reaction (2) will proceed in one direction until equilibrium is reached. The concentrations of carbon monoxide and carbon dioxide then present will be in the proportions that are inert with respect to

this steel and its oxide. If some carbon dioxide is introduced more steel will be oxidized, whereas if some carbon monoxide is introduced more oxide will be reduced. At each temperature the mixture that is in equilibrium with the steel may be determined and a curve plotted to show how the $\text{CO}_2 : \text{CO}$ equilibrium ratio changes with temperature. Such a curve is represented by No. 4 (Fig. 240). According to this curve a gas mixture in which the $\text{CO}_2 : \text{CO}$ ratio is 0.6 is in equilibrium with the alloy concerned at 750°C . If the temperature is raised or more carbon dioxide introduced the mixture becomes oxidizing, whereas if the

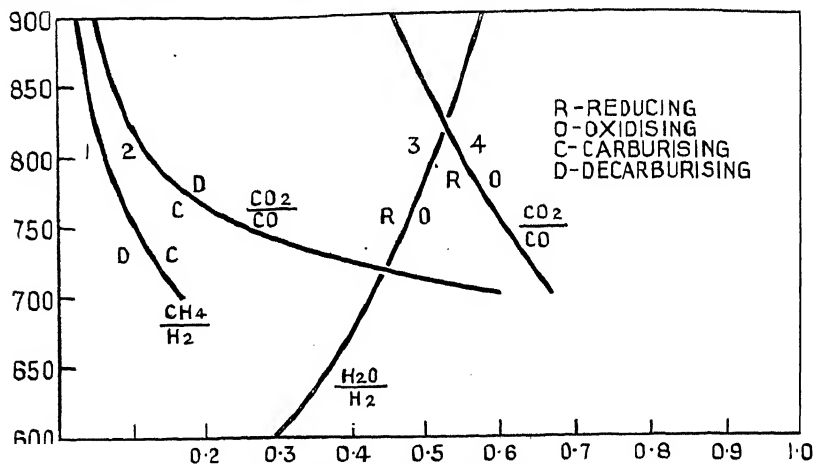


FIG. 240. Equilibrium ratios.

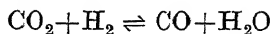
(Stansel.)

temperature is lowered or more carbon monoxide introduced it becomes reducing. In general, if the temperature and $\text{CO}_2 : \text{CO}$ ratio are such that they are represented by a point to the left of curve No. 4 the conditions are reducing, whereas if they are represented by a point to the right of curve No. 4 they are oxidizing.

In the same way the equilibrium ratios applicable to the other equations (1), (3), and (4) may be determined and represented by curves such as Nos. 3, 2, and 1 (Fig. 240). From such curves it is then possible to ascertain whether at a given temperature a given mixture of CO_2 and CO or of H_2O and H_2 is oxidizing or reducing or a given mixture of CO_2 and CO or CH_4 and H_2 carburizing or decarburizing. Thus at 800°C . if the ratio $\text{CO}_2 : \text{CO}$ is 0.6 the atmosphere is oxidizing and decarburizing, if the ratio is 0.4 it is reducing and decarburizing, while if the ratio is 0.1 it is reducing and carburizing. It will be noted that whereas a $\text{CO}_2 : \text{CO}$ ratio which is reducing at one temperature is reducing at all lower temperatures, a $\text{H}_2\text{O} : \text{H}_2$ ratio that is reducing at a high temperature may become oxidizing at a lower temperature.

In actual combustion atmospheres, however, all the above-mentioned gases are present together and owing to reactions between them, and

the several other factors, equilibrium curves like those shown in Fig. 240 have only an indirect bearing on practical conditions. When, for example, carbon monoxide and dioxide are present together with hydrogen and water vapour in a mixture the following reaction can occur:



As water vapour is a much more powerful oxidizing gas than carbon dioxide the progress of this reaction towards the right increases the oxidizing power of the atmosphere. Increase in the hydrogen content of a given mixture tends to cause this reaction to proceed towards the right, and consequently, increase in the proportion of the reducing gas hydrogen may under certain conditions increase the oxidizing power of an atmosphere. An example is given in Chapter VIII where it is shown that when hydrogen was added to a carbon dioxide atmosphere the rate of oxidation increased and reached a maximum at 26 per cent. of hydrogen when the rate of oxidation was 3.5 times as rapid as in carbon dioxide. Another example of the mutual effect of gases in a complex mixture is provided by the influence of water vapour on the decarburizing effect of hydrogen. In equation (4) which represents the carburizing-decarburizing relations between hydrogen and methane, water vapour does not appear, but its presence is required to promote rapid decarburization. The decarburizing effect of dry hydrogen is so slight that high carbon steels can be safely heated in it providing that there is no oxide present with which the hydrogen can combine to form water vapour. This, however, is not of much practical importance in view of the difficulty of preventing completely the presence of water vapour which promotes rapid decarburization. Its effect in this connexion is probably due to the fact that nascent hydrogen is required for decarburization and is more readily produced by the adsorption of water vapour than by that of hydrogen. Thus the actual decarburizer is water vapour and the function of the hydrogen is to keep up the supply of this gas by combining with the oxygen liberated when the water vapour combines with carbon to form methane. This is an indication of the kind of limitations to which the equations 1 to 4 are subject; they do not necessarily express what occurs, but only show which gases may be regarded as acting in pairs. A third example of the mutual effect of gases is provided by the influence of sulphur dioxide in stimulating oxidation generally.

If it is supposed that the equilibrium conditions between a given steel and all sorts of mixtures of furnace gases were worked out so that it would be possible to ascertain from the analysis of a given mixture whether it was oxidizing and decarburizing, reducing and decarburizing, or reducing and carburizing, numerous other factors would still have to be taken into account in practice. In the first place, the equilibrium would alter with the composition of the steel, e.g. the rate of oxidation tends to decrease and that of decarburization to increase with increase

in carbon content. Secondly, the amount of oxidation and/or decarburization taking place would tend to increase with temperature and time in any atmosphere capable of producing these effects, and thirdly, the rate at which the gas flowed over the metal surface might have an effect. In practice, therefore, the control of combustion atmospheres is largely an empirical problem, i.e. when a given fuel is being used in heating steel of a given composition at a given temperature, the air and fuel ratios are adjusted until the amount of decarburization and oxidation are decreased as far as is considered necessary, or as far as is consistent with maintaining the required thermal efficiency.

Owing to the variety of gases in combustion atmospheres these may be adjusted to be oxidizing or reducing, decarburizing or carburizing by altering the proportions of the different gases present. A reducing atmosphere may be used to remove oxide previously produced, but in general its advantage is that it does not oxidize and may therefore be considered as inert in this respect. Such an atmosphere may, however, decarburize and, in fact, as there is no oxidation taking place at the same time to remove the decarburized layer it produces the most marked decarburization. If this is to be prevented the atmosphere must be made carburizing. It follows therefore that a really neutral atmosphere cannot be maintained in a furnace in which the products of combustion are in contact with the steel. What is described as a neutral atmosphere is one which at the temperature used and during the period of heating employed does not produce a marked amount of oxidation, decarburization, or carburization. In general, the control of combustion atmospheres is resorted to to decrease the amount of oxidation, and when it is desired to prevent oxidation and decarburization artificial atmospheres are used. One reason for this is that combustion atmospheres are difficult to control exactly, another is the need for maintaining thermal efficiency. At the temperatures used in tempering, i.e. up to 650°C ., and low-temperature annealing, i.e. up to 680°C ., the rates of oxidation and decarburization are slow and a high degree of thermal efficiency in combustion is not required. In these treatments oxidation and decarburization may be almost entirely prevented by control of the combustion atmospheres. At the temperatures used in hardening (750 – 850°C .), full annealing and normalizing (840 – 920°C .), oxidation and decarburization take place more rapidly, and in addition greater thermal efficiency is required, and this applies in a very pronounced degree at the temperatures used in heating for working ($1,250$ – $1,320^{\circ}\text{C}$.). To prevent oxidation the concentration of the combustible gases carbon monoxide and hydrogen must be increased at the expense of the concentrations of carbon dioxide and water vapour, and this means that the fuel is only partly burnt. The general question then is, can the composition of the atmosphere be adjusted to the required extent without making it impossible to reach the required temperature? This depends on the amount of carbon monoxide and hydrogen required

to prevent oxidation and on the extent to which restricted combustion is possible.

Several investigations have been carried out in order to discover the amounts of carbon monoxide and hydrogen that must be present in mixtures with carbon dioxide and water vapour to restrict oxidation to different extents or prevent it altogether. Thus under one set of conditions it was found that in the range 800–1,000° C. an atmosphere containing 2 per cent. of carbon monoxide oxidized at one-third the rate of a 'neutral' atmosphere, whereas one containing 14 per cent. oxidized at one-sixth the rate. In the range 1,100–1,350° C., however, 13 per cent. of carbon monoxide was required to reduce the rate of oxidation to one-third of that of a 'neutral' atmosphere. As explained in Chapter VIII, Cobb and his collaborators studied the effects of adding hydrogen and carbon monoxide to combustion atmospheres and found that the amounts of these gases required to prevent oxidation at 1,000° C. were larger than could be obtained in ordinary practice when the heating value of the fuel had to be taken into account. In general, therefore, it may be said that at all temperatures oxidation may be restricted by controlling combustion atmospheres, but except at temperatures such as those used in tempering and low-temperature annealing it cannot be reduced to a very small amount.

We may turn now to other methods of preventing oxidation and decarburization. The oldest of these is that known as pot-annealing which has long been used in the annealing of strip, sheet, and wire when a bright surface is required. This is carried out by packing the material to be annealed in heavy cast-iron or steel boxes along with some material which when heated combines readily with oxygen or other oxidizing gases, e.g. charcoal or cast-iron borings. This method has proved very successful in preventing oxidation, but it has several disadvantages arising from the trouble involved in packing and the time and thermal energy required to thoroughly heat the boxes and packing materials. A further development of this method consisted in introducing a non-oxidizing gas into the boxes and thus providing an artificial atmosphere, but this innovation brings pot-annealing into the class of operations now to be described. A process similar to pot-annealing is the use of what is known as a diamond block in the heating of tools. This block is made up of carbonaceous materials and contains a slot into which the tools are inserted. When placed in a muffle furnace at the heat-treating temperature the block is slowly consumed and the products of its combustion maintain in the slot an atmosphere containing sufficient carbon monoxide to prevent oxidation and decarburization. Similar results may in general be obtained by placing charcoal, graphite, or cast-iron chips in muffle furnaces in which the atmosphere is fairly stagnant.

During the last ten years the use of artificial atmospheres has been adopted to an increasing extent in order to prevent oxidation and decarburization in such operations as the hardening of tools and springs,

the annealing of cold-worked strip, sheets, pressings, tubes, and wire and the heat treatment of carburized parts. When such atmospheres are used there must be no admission of air or products of combustion to the chamber where the metal is heated, and the furnace thus becomes a container for the metal and the artificial atmosphere. Gas may be used for heating if the working chamber is a metallic or refractory muffle heated from outside, or if the heating gases burn inside tubes made of heat-resisting alloy, but most of the furnaces used with artificial atmospheres are electric. In the construction of furnaces of this kind provision must be made for introducing and withdrawing the work without permitting air to enter. In batch furnaces heated and cooled with the charge, the air may be swept out before heating begins, and thereafter ingress of air through any small openings may be prevented by maintaining a positive pressure inside. When parts have to be introduced and withdrawn while the furnace is kept at the operating temperature the entrance of air is usually prevented by means of a gas 'curtain' which is a gas flame that burns in front of the door-opening and is controlled by the movement of the door. In continuous furnaces, which have a permanent opening at each end, ingress of air is prevented by restricting the size of these openings as far as possible and maintaining a positive pressure inside. When such furnaces are used with artificial atmospheres a long cooling zone must be provided in order to prevent the stock coming out into the air while still hot. This does not apply, however, to continuous hardening furnaces from which the stock is discharged into the quenching medium.

Being inert to iron and carbon, nitrogen would appear to be a very suitable gas for an artificial atmosphere, but it is difficult to ensure that the gas is free from oxygen and water vapour and that no air enters the furnace, and as no reducing gas is present to counteract the effect of these an appreciable amount of oxidation may occur. Furthermore, nitrogen purchased in cylinders is costly. Provided that it is thoroughly dried, hydrogen is another possible gas. When purchased in cylinders it is expensive, but it can be obtained more cheaply by electrolysis once the necessary plant has been installed. Mixtures of hydrogen and nitrogen have, however, substantial advantages over either gas separately in that there is no danger of oxidation by small quantities of oxygen or water vapour and the danger of decarburization is less. Furthermore, a mixture of these gases can be obtained conveniently and relatively cheaply by the cracking of anhydrous liquid ammonia. This is obtained in cylinders and a large volume of gas is produced from a relatively small quantity of liquid when the ammonia is cracked, i.e. dissociated into a mixture of nitrogen and hydrogen, thus, $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$. In using such a mixture containing 25 per cent. of hydrogen there is some risk of explosion, but the gas may be burned with a deficiency of air to convert most of the hydrogen to water vapour. In this way the volume of gas is increased with nitrogen from the air, and

after the water vapour has been removed by condensation a mixture of nitrogen and hydrogen containing less than 10 per cent. of hydrogen is obtained. More complete drying can be obtained by desiccation over calcium chloride after condensation.

Robiette (274) has calculated the approximate costs of atmospheres of the above types. He states in the first place that when heating is carried out in closed containers such as electric furnaces of the batch type the consumption of gas is about 75 to 150 cu. ft. per ton of metal treated, whereas when it is carried out in continuous furnaces which permit the escape of gas from the ends it is about 500 to 1,500 cu. ft. per ton of metal. Hydrogen and nitrogen in cylinders cost about 50s. per 1,000 cu. ft. Electrolytic hydrogen after the generating plant has been installed costs about 5s. per 1,000 cu. ft., dissociated ammonia about 26s., and the atmosphere obtained by the partial combustion of this gas 10s. to 14s. per 1,000 cu. ft.

Cheaper atmospheres may be obtained by the partial combustion of coal-, producer-, or natural-gas or of butane (C_4H_{10}) which is a hydrocarbon by-product of the cracking of crude oil and is available as an easily transported, easily gasifiable liquid, comparatively free from sulphur. The gas mixtures obtainable in this way resemble those that could be produced in furnaces operating with a deficiency of air if thermal efficiency did not have to be considered and purification were possible. The most convenient source of this kind of atmosphere is butane. When completely burned it yields a mixture of nitrogen, carbon dioxide, and water vapour which after condensation and drying consists of 87 per cent. nitrogen and 13 per cent. of carbon dioxide. Owing to the absence of reducing agents such an atmosphere will oxidize heated steel, and more useful atmospheres can be obtained by partial combustion which yields an atmosphere consisting of nitrogen, hydrogen, water vapour, carbon monoxide, carbon dioxide, and a small percentage of hydrocarbons. From this the water vapour may be removed by condensation and drying and a reducing atmosphere is thus obtained. Similar atmospheres, containing nitrogen, hydrogen, hydrocarbons, carbon monoxide, and carbon dioxide can be obtained by the partial combustion of industrial gases followed by drying, and the air supply can be adjusted so that definitely reducing conditions are produced. It is more difficult, however, to prevent decarburization and carburization, and usually the one or the other must be allowed to take place to a slight extent. The advantage of butane over industrial gases is the absence of sulphur compounds in the atmosphere produced. Even when these do not appreciably affect the metal undergoing treatment, they have a pronounced effect on the nickel-chromium alloys used as resistors in electric furnaces and this is most severe when the atmosphere is reducing. Consequently, for the successful use of atmospheres obtained by the partial combustion of fuel-gases means of removing sulphur compounds must be adopted.

In the annealing or normalizing of cold-worked products the object of using artificial atmospheres is to eliminate oxidation and such small amounts of decarburization as occur can usually be permitted. In the heat treatment of tools and springs, however, it is even more important to prevent decarburization than scaling. If we start with an atmosphere that produces decarburization, and increase the proportion of oxidizing gases, then oxidation may be made to take place more rapidly than decarburization so that a film of scale is produced instead of a decarburized surface. If, however, we increase the content of carbon monoxide and hydrocarbons, a carburized surface is liable to be produced. It is thus very difficult, if not impossible, to obtain an absolutely inert atmosphere. For practical purposes what constitutes an inert atmosphere depends on the time and temperature of heating and the amount of oxidation, decarburization, or carburization that may be permitted, and thus tools and similar articles are frequently heated in atmospheres that permit one or other of these changes to take place to a slight extent. Several methods have been proposed, however, for further decreasing the extent of these changes. In heating high-speed tools for hardening they are first preheated at 845–930° C. before being raised to the hardening temperature of 1,260–1,290° C. This is done to decrease the internal stress that would result from placing the cold tools into a furnace at the higher temperature. As two furnaces are used, an opportunity is provided of employing complementary atmospheres. Thus slight oxidation may be permitted during pre-heating and the scale removed by using a reducing atmosphere for hardening, or pre-heating may be carried out in a reducing (and decarburizing) atmosphere and the decarburized layer removed as scale by maintaining an oxidizing atmosphere in the hardening furnace, or finally, one atmosphere may be made slightly carburizing and the other slightly decarburizing. For the heat-treatment of springs a carburizing atmosphere is usually recommended.

The hardening temperature of high-speed steel is exceptionally high, but for the hardening (and tempering) of carbon-steel tools, and certain alloy-steel tools, baths of oil, lead, or salt are extensively used. These baths can readily be maintained at the desired temperature, and articles of any shape uniformly heated without oxidation. Oil baths are useful only for tempering, as they cannot be used above 260° C. Lead baths may be used for all temperatures above the melting-point of lead (327° C.) and below the temperature at which the rate of oxidation of lead becomes so rapid that its use is inexpedient, i.e. about 930° C. Salt baths of different compositions are available for use over a wide range of temperature. For tempering, baths which operate in the range between 150° and 600° C. are obtained by the use of sodium nitrate and potassium nitrate. These salts melt at about 310° C. and 340° C. respectively, but mixtures melt at lower temperatures, and the eutectic mixture consisting of 55 per cent. sodium and 45 per cent.

potassium nitrate melts at 205° C. By the addition of sodium nitrite still lower temperatures may be obtained. For the hardening of steels, except high-speed steels, two alternative types of bath which work in the range of temperature between 650° and 930° C. are available. In order to prevent any surface decarburization those containing sodium- or potassium cyanide are frequently employed. The usual mixture consists of sodium carbonate and sodium chloride in equal quantities mixed with from 10 to 45 per cent. of sodium cyanide. As sodium cyanide is a carburizing compound such baths are liable to produce an increase in the carbon content of the surface of the steel. Generally this is unobjectionable, but where the formation of a 'case' cannot be permitted, mixtures of sodium, potassium, barium, and calcium chlorides may be employed. Many different mixtures of these salts have been recommended but one containing the chlorides of calcium, sodium, and barium in equal proportions is much favoured.

ATMOSPHERE CONTROL IN HEATING NON-FERROUS METALS

Lead, zinc, and tin and alloys based on them are not subjected to heating operations, and attention may therefore be confined to aluminium, copper, and nickel, and their alloys. Of these metals aluminium and its alloys are unique in that, whereas thin oxide films are readily formed even on exposure to air at ordinary temperature they are so impervious to the diffusion of oxygen that they never become very thick. These films are a source of trouble in working, electroplating, and soldering, but they do not destroy the appearance of the metal. In any case it would be extremely difficult to prevent their formation or to remove them when formed, and consequently atmosphere control designed to prevent oxidation and methods of removing oxide are not involved in the treatment of aluminium and its alloys. It follows, therefore, that so far as the common non-ferrous metals are concerned, atmosphere control is only important in connexion with copper and its alloys brass and bronze, and nickel and its alloys copper-nickel, nickel-chromium, and the nickel-silvers. The heat treatments to which these metals are subjected are heating for hot-working and annealing in connexion with cold-working. In operations of the former kind the atmosphere is controlled in the same way as in corresponding operations on steel, i.e. no attempt is made to prevent oxidation entirely, and, as a thin tenacious oxide will cause more trouble than a thicker and looser layer, heating is generally carried out in combustion atmospheres adjusted so as to produce the minimum amount of scale consistent with free scaling. In annealing in connexion with cold-working there are two alternative procedures, either the atmosphere may be adjusted so as to restrict scaling while forming an easily detachable scale, which is removed by pickling after each annealing,

or it may be controlled so as to completely prevent oxidation and eliminate the need for pickling. The latter procedure is now being adopted to an increasing extent.

The number of annealing treatments which are required in the manufacture of a given rolled, drawn, or pressed article varies with the amount of change in shape that has to be produced in the cold and the properties finally required, but in general cold-worked products require to be annealed at some intermediate stage in manufacture and again before going into service. If these operations are carried out in an atmosphere that permits oxidation, the scale must be removed before the article goes into service or is subjected to further working. This is usually done by pickling, i.e. immersion in acid, as described in a later section. The process has several disadvantages. The plant occupies a considerable amount of space and the operation requires a certain time. Furthermore, a lot of handling is involved in passing the stock through the pickling bath and the subsequent washing processes. As the scale formed is rarely of a uniform thickness, and as pickling produces an etched rather than a lustrous effect, the surface obtained in this way is not very satisfactory, and when a good surface is required, polishing, or in certain cases final cold-working, is necessary to obtain it. These difficulties are avoided if the annealing operations are carried out in atmospheres that do not oxidize the metal, and annealing under such conditions is known as 'bright' annealing.

In this process the object is not to restrict oxidation, but to prevent it altogether, for quite thin oxide films interfere with working and impair the appearance of the metal by developing interference colours. In view of this, great importance sometimes attaches to what may appear to be relatively unimportant factors. In using artificial atmospheres it is essential to provide at least a slight flow of gas, and even a small amount of an oxidizing constituent may produce an appreciable amount of oxidation because the supply is continuously renewed. Thus, e.g. the amount of oxide produced on copper in a nitrogen-hydrogen atmosphere containing 0.1 per cent. of oxygen is sufficient to spoil the effect of heating in this atmosphere because interference-colour films result. Again, many metals when heated evolve gas, and the amount of this may be sufficient to spoil a treatment unless the atmosphere supplied is sufficiently reducing to reduce any oxide formed by evolved gases. Thus brass when heated gives off occluded gas containing appreciable amounts of oxygen and carbon dioxide, and if it is annealed in a neutral atmosphere, e.g. nitrogen, it is oxidized. For this reason the nitrogen must be mixed with a sufficient quantity of a reducing gas, e.g. hydrogen. Furthermore, atmospheres that are non-oxidizing at a high temperature may become oxidizing at a lower temperature, and consequently care must be taken that the atmosphere used remains non-oxidizing down to the lowest temperature at which oxide can form. Finally, various kinds of lubricants are used in connexion with cold-

working operations, and when these are left on the surface of the metal entering the annealing furnace they may give rise to surface defects of various kinds, e.g. oxidation by free oxygen liberated from organic matter in the lubricant or by water from soluble oils, or staining by deposition of carbon produced by cracking of the lubricant. On this account oily lubricants should be removed in a degreasing plant before annealing, and soluble oils should be removed by washing and drying.

For the bright annealing of non-ferrous metals, atmospheres similar to those used in connexion with steel are employed, and in addition steam is suitable for the annealing of copper. This is possible because copper, unlike steel, is not oxidized by this gas, and the process is one of the longest-established methods of bright annealing. It is essential that the steam be free from oxygen otherwise oxidation will occur. The chief difficulty is to avoid condensation of moisture on the copper during heating or cooling, for this results in staining, and although steam annealing has proved very satisfactory in many respects it has recently been replaced to some extent by annealing in reducing atmospheres. With these, however, the danger of 'gassing' arises. Tough-pitch copper contains a certain amount of oxide, and when the metal is annealed in a reducing atmosphere hydrogen diffuses into it and combines with the oxide to form steam. This cannot escape by diffusion and builds up a pressure at the crystal boundaries and causes brittleness. Gassing does not occur, however, if the atmosphere contains less than 10 per cent. of reducing gases, and consequently the atmosphere obtained by the almost complete combustion of the mixture produced by cracking ammonia is suitable for the bright annealing of copper. This also applies to the atmospheres obtained by the substantially complete combustion of butane or town gas.

The problem of bright annealing brass is complicated by the volatilization of zinc from the surface. This occurs readily in the annealing range (550–800° C.) and is much more pronounced in reducing than in oxidizing atmospheres. Owing to the oxidizing gases evolved by heated brass a neutral atmosphere (e.g. nitrogen) is not suitable, and steam is unsuitable for the same reason as well as for the fact that zinc can dissociate this gas. Consequently, atmospheres containing hydrogen and free from appreciable quantities of oxygen, carbon dioxide, and steam are required. The volatilization of zinc may be minimized by passing the gas over heated zinc or brass turnings so as to partially saturate it with zinc vapour.

The bright annealing of nickel and copper-nickel alloys is comparatively easy in so far as the prevention of oxidation is concerned, for these metals are not oxidized by mixtures containing carbon dioxide and water vapour so long as hydrogen and carbon monoxide are present in suitable proportions. From this point of view therefore appropriate atmospheres are obtainable by the partial combustion of fuel gas. Nickel and its alloys, are however, susceptible to deterioration when

heated in reducing atmospheres containing sulphur, and therefore for their satisfactory treatment the gas must be obtained from a sulphur-free source, i.e. ammonia or butane, or the sulphur must be removed. Until recently the former method had to be adopted, but an economical and satisfactory method of eliminating sulphur from partly burned town gas with bog iron ore has now been developed. In the bright annealing of nickel silvers (Cu-Ni-Zn alloys) the volatilization of zinc has to be considered, and the bright annealing of nickel-chromium alloys is rendered difficult by the presence of chromium which has a high affinity for oxygen and may be oxidized by water vapour or carbon dioxide besides combining with nitrogen to form nitrides. The most suitable gas for bright annealing nickel-chromium alloys is hydrogen, but the hydrogen-nitrogen mixture obtained by dissociating ammonia can also be used unless the duration of heating is very long.

GENERAL EFFECTS OF HEAT TREATMENT

A complete heat-treating cycle consists of three stages: heating, maintenance at temperature (i.e. soaking), and cooling. Sometimes the heating stage is eliminated, as when castings are taken from the mould when hot and transferred to an annealing furnace, or when ingots are transferred to a soaking pit shortly after they have solidified and there kept hot for working. This procedure may result in saving a certain amount of thermal energy, but it also prevents cracking during cooling, and eliminates the danger of the formation of clinks during heating again. In any case, except for the fact that rapid heating may lead to the development of clinks in large masses of hard metal, the heating stage does not produce any effects that are not produced to a greater extent while the metal is being soaked, and for this reason heating and soaking may be considered together in this section.

One of the most important effects of heating is that the metal becomes more plastic. This enables internal stress to be eliminated and facilitates working. All the other effects of heating (except reactions between the metal and its environment) depend on the existence of some constitutional or structural instability when heating begins or on transformations occurring in the solid metal. If, therefore, a metal that undergoes no transformations in the solid state is allowed to solidify under equilibrium conditions and is not deformed, it is possible to heat it again to near the melting-point without any changes taking place. If, however, any of these conditions are departed from, then heating cannot be carried beyond a certain limit without affecting the metal. The purpose of this section is to describe briefly the various types of changes that occur on heating metals that (a) are solidified under conditions that depart from equilibrium, (b) undergo transformations in the solid state, or (c) are subjected to deformation.

Attention may first be given to metals that undergo no transforma-

tions in the solid state, e.g. (a) pure metals that exist in one form only, (b) primary solid solutions belonging to completely miscible systems in which neither metal undergoes a polymorphic change, and (c) intermediate constituents that are stable at all temperatures below their melting-point. None of these metals undergoes a change on heating after casting if equilibrium conditions are realized during solidification. If, however, such conditions do not result, then heating can promote changes in primary solid solutions and intermediate constituents. In such phases a departure from equilibrium during solidification leads to a non-uniform distribution of the constituent elements, except in the case of intermediate constituents that have a narrow freezing range and a narrow composition range of stability. The heterogeneity thus produced is of two types: (1) variation in composition between different regions in each crystal, and (2) variations in composition between different regions in the alloy as a whole. Heating the alloy tends to eliminate this heterogeneity by permitting diffusion. As the distances over which diffusion must take place to eliminate partially or completely heterogeneity of the first type, are relatively small, this heterogeneity is affected in a pronounced degree by heating at temperatures near the solidus. The time required to produce substantial uniformity decreases as the temperature increases and as the initial heterogeneity decreases, but it varies considerably between one alloy and another, and in a solution consisting of several elements in one basis metal some of the elements may become uniformly distributed more rapidly than others. The distances over which diffusion must take place in order to reduce substantially heterogeneity of the second type are much greater, and this cannot in general be greatly altered by heating after casting.

Closely related to the above is the effect of heating on an alloy which under equilibrium conditions of solidification would consist of one constituent, but which under the conditions actually realized in practice may consist of two. When a copper-zinc alloy containing 30 per cent. of zinc is cooled rapidly, as in a small chill casting, it still consists only of the α -constituent (Fig. 129), but when one containing 35 per cent. of zinc is similarly cooled it consists of $\alpha + \beta$. When an alloy of the first type is heated, all that can take place is a redistribution of the zinc within the α -phase, resulting in greater homogeneity, but when an alloy of the second type is heated the uniform distribution of zinc that is then produced results in the disappearance of the β -phase. Similarly, in the copper-tin alloys (Fig. 517) the δ -constituent does not occur under equilibrium conditions unless the alloy contains 16 per cent. of tin, but in practice it occurs in castings of Admiralty gun-metal which contains only 10 per cent. of this metal. Heating such a casting at about 700° C. tends to bring about a uniform distribution of tin with the result that when it is again cooled the amount of δ is considerably less if it is not absent altogether. As the α -constituent is ductile while the δ is brittle, such a treatment has a considerable effect on the mechanical properties,

reducing the hardness and increasing the strength and ductility, but it is not resorted to in practice because gun-metal is used more because of its resistance to wear than because of its strength and ductility. Changes of this type may be produced in all sorts of alloys which when cast are not in a condition of equilibrium, and they occur regularly in the solution treatment of aluminium alloys. An alloy containing 4 per cent. of copper, for example, should be a solid solution if solidified under equilibrium conditions (Fig. 153), but in practice it contains free CuAl_2 , and during the solution treatment this is dissolved along with the CuAl_2 that separates from solution during cooling from the casting temperature to atmospheric temperature.

Besides producing heterogeneity in single phases and causing the appearance of constituents which under equilibrium conditions would be absent, rapid cooling through the range of solidification tends to increase the proportion of the phase that solidifies last. Thus in an alloy that consists under equilibrium conditions of primary crystals and a eutectic, increase in the rate of freezing will tend to increase the proportion of eutectic, while in an alloy that consists under equilibrium conditions of $\alpha + \beta$, increase in the rate of cooling will tend to increase the proportion of β . Heating after casting will, as in the previous examples, enable the alloy to change in the direction of equilibrium with the result that the relative proportions of the phases will alter.

The changes above described are due to the effect of heating in permitting metals that are not in a stable state to approach more closely to that condition. They are affected by the time and temperature of heating but not by the rate of cooling. Another change that may be classified with them is the spheroidization and coalescence of a dispersed constituent, for although this can occur in alloys that are in what is usually regarded as a stable state, the fact that it does occur indicates that even when constitutional equilibrium is achieved certain structural changes can still occur. The spheroidization and globularization of pearlite were described in Chapter VI, but as this is a eutectoid formed by a transformation in the solid it has no direct bearing on the subject under consideration. Similar changes may, however, take place in eutectics, and one of the best examples is provided by the eutectic in the aluminium-silicon alloys. In this eutectic the silicon occurs in the form of small angular dispersed particles in the alloy as cast. Heating after casting permits them to change into globules under the action of surface tension and allows some to grow at the expense of others by a process of solution and redeposition (i.e. coalescence). This change proceeds progressively as the temperature is raised or the time of heating prolonged, and results in a softening of the alloy. Similar changes may occur in many alloys containing a eutectic, but the rate at which they occur depends to some extent on the structure of the eutectic. If one of the constituents is dispersed throughout the other, changes of this type occur easily, whereas, with the other types of eutectic structure

they take place less readily. In these latter cases spheroidization and globularization, are promoted by working before heating. Similar changes also take place when eutectoids are heated, or worked and heated, and when supersaturated solid solutions retained by rapid cooling are heated as, e.g. in the tempering of martensite or the precipitation of CuAl_2 from enforced solution in aluminium.

Attention may now be given to the changes that occur when metals that undergo changes in the solid state are heated, and as they have already been considered in Chapter VI they need only be mentioned briefly here. In this connexion three aspects have to be noted: (1) the condition of the metal when heating begins, (2) the effect of the heating, and (3) the effect of the subsequent cooling.

When a pure metal that undergoes a polymorphic change is cooling from the freezing temperature a complete recrystallization occurs as it passes through the transformation range. The microstructure at atmospheric temperature then depends on the structure formed at solidification and the way in which the polymorphic recrystallization occurs. These in turn depend on the rates of cooling through the freezing and transformation range respectively. If the metal is again heated it transforms in the reverse direction on passing through the transformation range, recrystallization again occurs, and the microstructure obtained on cooling now depends on the temperature of heating (and to a less extent on the time) and the subsequent rate of cooling. Thus when pure iron is heated through the range of the $\alpha \rightarrow \gamma$ transformation small crystals of γ -iron are first produced and these proceed to increase in size as the temperature is raised. With a given rate of cooling the α -iron crystals subsequently formed increase in size with the γ -iron crystals. Beginning with γ -iron crystals of a given size, however, the size of the α -iron crystals formed from them may be decreased by increasing the rate of cooling. Consequently, by heating to different temperatures above the transformation temperature and cooling at different rates the size, shape, and general arrangement of the crystals in pure iron can be varied within wide limits.

In alloy systems of Types 3A, 3B, and 4 (Table 24, page 277) changes in solid solubility occur on cooling from the freezing-point to atmospheric temperature. On heating again they take place in the reverse direction. Thus a silver-copper alloy (Type 3A), containing, say, 20 per cent. of copper, consists at solidification of two solid solutions, one rich in silver and containing 8.8 per cent. of copper and the other rich in copper and containing 8.0 per cent. of silver (Fig. 152). As the alloy cools, the compositions alter by diffusion, i.e. copper diffuses from the silver-rich to the copper-rich phase and silver from the copper-rich to the silver-rich phase. If the rate of cooling permits equilibrium to be established, then at atmospheric temperature the silver-rich solid solution contains 0.3 per cent. of copper and the copper-rich contains

0.1 per cent. of silver. If the conditions do not permit equilibrium to be established, the silver-rich solid solution will contain something between 0.3 and 8.8 per cent. of copper and the copper-rich will contain something between 0.1 and 8.0 per cent. of silver. If the alloy is heated after casting to a temperature near the eutectic temperature, the conditions existing at solidification may be restored. It is then possible by cooling more slowly than before to approach more nearly to equilibrium at atmospheric temperature, or by cooling more rapidly than before to depart more extensively from equilibrium. Thus, whatever the distribution of silver and copper between the two phases in the alloy as cast, it is possible by heating to near the eutectic temperature and cooling at different rates to obtain at atmospheric temperature a condition approaching equilibrium at this temperature or to retain one approaching equilibrium at the eutectic temperature.

Similar results may be obtained with alloys belonging to systems of Type 3B and 4 (Table 24). Thus an aluminium-copper alloy containing less than 5.65 per cent. of copper consists when solidified under equilibrium conditions of a solid solution of copper in aluminium (Fig. 153), while one containing between 5.65 and 33 per cent. of copper consists of primary crystals of this solid solution and a eutectic of this and CuAl_2 . On cooling from the freezing temperature the solubility of copper in aluminium diminishes. If the rate of cooling permits equilibrium to be realized then only 0.5 per cent. of copper remains in solution at atmospheric temperature and the remainder is present as CuAl_2 . If the rate of cooling is faster than this, more copper is retained in solid solution, and in general the amount so retained increases with the rate of cooling from the freezing temperature. Whatever the amount of copper retained in solution on cooling after casting, it can be subsequently adjusted by heating and cooling. Thus by heating at a temperature near the eutectic temperature over 5 per cent. of copper can be taken into solution in the aluminium. By cooling more slowly than before the amount retained in solution at atmospheric temperature can be made less than before; by cooling more rapidly it can be made more, up to the limit of the amount dissolved at the heating temperature.

In many alloys changes from one constituent to another occur. Thus a copper-zinc alloy containing 37.5 per cent. of zinc (Fig. 129) solidifies as the β -constituent. As it cools α begins to form. Over a certain range of temperature the alloy consists of $\alpha + \beta$ and below this of α alone. These changes are affected, however, by the rate of cooling, and whatever the constitution of the alloy as cast, it is possible by heating into the β -range to retain it in the β , $\alpha + \beta$, or α condition by adjusting the rate of cooling. In the other alloys, e.g. iron-carbon, copper-tin, and copper-aluminium, a phase stable at a high temperature undergoes an inversion, and a eutectoid consisting of two constituents is formed. Again, whatever the condition of the alloy as originally cooled, its constitution and structure may be altered by heating to different temperatures above

the eutectoid temperature and cooling at different rates. This will be further discussed presently.

In the foregoing consideration of the effects of heating and cooling on alloys that undergo changes in the solid it has been assumed that once the alloy has been heated to obtain the condition stable at the high temperature it is possible, by varying the cooling rate, to retain at atmospheric temperature any condition between that of equilibrium at that temperature and that at the high temperature. In general, however, even with the slowest cooling it is impossible to obtain at atmospheric temperature the exact conditions represented by the constitutional diagrams, for these are determined by means of prolonged soaking experiments. Furthermore, even with the most rapid cooling it is sometimes impossible to retain at atmospheric temperature the conditions existing at high temperature. Thus it should be said that when an alloy is heated so as to obtain the condition stable at high temperature, it is possible by progressively decreasing the rate of cooling to retain at atmospheric temperature conditions approaching nearer and nearer to equilibrium at this temperature, and by progressively increasing the rate of cooling to retain conditions approaching nearer and nearer to those existing at the high temperature. In some cases, however, the effects of varying the rate of cooling are complicated by the fact that suppression of the changes that normally take place does not result in the retention of the phase stable at high temperature. In other words, when the normal changes are suppressed by rapid cooling another kind of change occurs, and it is the product of this that is retained at atmospheric temperature. This occurs in the case of steel, and the heating and cooling of this alloy may be described briefly in order to illustrate the effect of such operations on a metal that undergoes a change from one constituent to another, a change in solid solubility and a eutectoid change, and in which suppression of the normal transformations gives rise to a new transformation. The subject is more fully discussed in Chapters VI and XI.

Steel may be described in the first instance as an iron-carbon alloy containing not more than 1.7 per cent. of carbon, and the diagram representing the normal changes that occur in the solid is shown in Fig. 239. Above the line *GSE* it consists of austenite, viz. a solid solution of carbon in γ -iron. If the steel contains less than 0.87 per cent. of carbon the austenite begins to transform when cooled to the appropriate point on the line *GS*. Ferrite, which is α -iron containing very little carbon, begins to form, and this continues while the temperature falls. Meanwhile the carbon content of the austenite is increased by the carbon rejected by the ferrite, and by the time the temperature has fallen to 725° C. the austenite has reached the composition *S*. The transformation of the austenite is then completed by the simultaneous formation of ferrite and cementite, i.e. the eutectoid reaction which leads to the formation of pearlite. If the steel contains more than 0.87 per cent. of

carbon, the austenite begins to transform when cooled to the appropriate point on the line ES . Carbon begins to be deposited from solution as cementite (Fe_3C). This continues as the temperature falls and the carbon content of the austenite diminishes. At $725^\circ C$. the austenite reaches the composition S and its transformation is completed by the formation of pearlite. Below $725^\circ C$. a steel which contains 0.87 per cent. of carbon consists of pearlite. Steels containing less carbon consist of pearlite and ferrite, and the amount of the latter increases as the carbon content decreases. Steels containing more carbon consist of pearlite and cementite and the amount of the latter increases with the carbon content. No further change takes place during cooling.

During heating the normal changes take place in the reverse direction, and the constitution and structure of steel as cast may be extensively modified by heating to different temperatures and cooling at different rates. In general the austenite grains are large in cast steel, and on cooling through the critical range (i.e. between lines GSE and PS , Fig. 239) a coarse ferrite-pearlite or cementite-pearlite structure is produced. If the steel is heated again the structures formed on cooling revert to austenite, and when the critical range has just been passed the austenite grains are small. On cooling from such a temperature a fine ferrite-pearlite structure may be obtained. As heating proceeds above the critical range the austenite grains increase in size, and the structures obtained by cooling at a given rate become coarser. If, however, a constant heating temperature is adopted and the rate of cooling varied, then the following alterations in structure may be obtained.

Firstly, increasing the rate of cooling lowers the temperature at which the normal changes begin on cooling and alters the conditions under which they take place. As a result of this a progressive increase in the rate of cooling is accompanied by (a) progressive refinement of the general ferrite-pearlite or cementite-pearlite structure, (b) progressive refinement of the lamellae in pearlite, and (c) an increase in the relative amount of pearlite in a steel of a given composition. Secondly, when a certain critical rate of cooling is exceeded, the formation of ferrite, cementite, and pearlite is suppressed, and the austenite cools through the critical range unchanged. At a lower temperature, however, another change begins. The iron transforms from the γ - to the α -form with the carbon still in solution, and the product of this change, i.e. a solid solution of carbon in α -iron, is called martensite. The temperature at which the formation of martensite begins decreases as the carbon content increases (Fig. 181). In steels containing less than 0.9 per cent. of carbon the austenite \rightarrow martensite transformation is substantially completed above atmospheric temperature. As the carbon content increases above this the change is interrupted at progressively earlier stages by the alloy reaching atmospheric temperature. Consequently, in rapidly cooled steels the amount of austenite retained by rapid cooling increases as the carbon content rises from 0.9 to 1.7 per cent.

It will be seen from the above that substantial alterations in the constitution and structure of steel can be obtained by heating and cooling under controlled conditions. In practice, however, it is not possible to obtain all the results obtainable in the heat treatment of small specimens under laboratory conditions. It is, for example, difficult to heat comparatively large masses of steels of different composition at temperatures just above the critical range in order to obtain small austenite grains. Furthermore, as the rate of cooling is so much affected by the size of the piece to be cooled it is impossible to adjust correctly the rate of cooling. To overcome these difficulties alloying elements are used, and as will be shown in Chapter XIII it is customary to adopt more or less standard methods of treatment and to control the result by varying the composition. The elements most widely used are nickel, chromium, manganese, and molybdenum, and further effects of these and of other elements are discussed in the chapter referred to, but in the meantime it will suffice to say that alloying elements have the following effects:

1. They decrease the rate of austenite grain growth above the critical range and make it easier to obtain fine grains.
2. They refine the ferrite-pearlite structure and the lamellae in pearlite.
3. They increase the relative amount of pearlite in a steel of given carbon content cooled at a given rate.
4. They reduce the rate of cooling necessary to obtain martensite, and thus make it possible to retain this constituent in larger masses of steel and by cooling in oil or air instead of water.
5. They facilitate the retention of austenite, and when present in suitable amounts enable steels to be retained in the austenitic condition at atmospheric temperature.

Any constitutional or structural condition retained at atmospheric temperature by means of rapid cooling is unstable at this temperature. Owing to the immobility that prevails at this temperature, however, an unstable condition may persist indefinitely. Alternatively, some change may proceed, either comparatively rapidly or extremely slowly. Raising the temperature facilitates the progress of such a change and permits (a) persistent phases to decompose, (b) those that change slowly at atmospheric temperature to change more rapidly, and (c) those that change rapidly at atmospheric temperature to change even more quickly. The distinction between persistence and non-persistence at atmospheric or any other temperature depends on the rate of the change in relation to the time over which the alloy may be studied and the sensitivity of the methods available for detecting the change. Consequently, the classification of phases as persistent and non-persistent is rather arbitrary, but for practical and descriptive purposes it is necessary. Thus austenite retained at atmospheric temperature by the addition of manganese, nickel, or nickel+chromium and rapid cooling is said to be persistent at this temperature unless it is deformed. The

solid solution retained by quenching aluminium-copper alloys is, however, not persistent and changes at an appreciable rate at atmospheric temperature. Martensite is intermediate between these two types. When freshly retained by rapid cooling it undergoes a certain amount of decomposition, but the amount of this is small and proceeds at a diminishing rate so that a persistent state is soon reached. Raising the temperature increases the rate of all changes of this kind, and a heating operation carried out with this purpose is known as tempering in the case of steel and temper-hardening in the case of aluminium-copper and numerous other alloys. Lowering the temperature tends, in general, to decrease the rate of such changes, so that aluminium-copper alloys that change fairly rapidly at atmospheric temperature are persistent at substantially lower temperatures. It should be noted, however, that although the decomposition of martensite and austenite are phenomena of the type under consideration, the change from austenite to martensite is of quite a different character. Thus when a steel containing 1.7 per cent. of carbon is quenched from 1,100° C. in water and retained at atmospheric temperature as a mixture of martensite and austenite, the retention of this austenite is due to this temperature being an intermediate point in the austenite \rightarrow martensite range (Fig. 181). On further cooling the change continues. In certain alloy steels a completely austenitic condition may be retained at atmospheric temperature because the upper limit of the austenite \rightarrow martensite range is below it. On further cooling, however, martensite may begin to form.

The phases retained at atmospheric temperature by rapid cooling are solid solutions and the mechanism of their decomposition is dealt with in Chapter VI. Briefly, this involves precipitation of the constituent retained in solid solution, but this is preceded by a change leading to it, and followed, under suitable conditions, by spheroidization and coalescence of the precipitated phase. In the case of austenite, precipitation is also accompanied by a change in the iron from the γ to the α form.

In general we may say that any condition that is established at a high temperature will have a range of persistence at a lower temperature, but to realize this it is necessary to be able to cool it sufficiently rapidly through the range between the lower limit of stability and the upper limit of persistence, and subsequently to maintain it below the upper limit of persistence. When austenite contains a sufficient amount of manganese, nickel, or nickel-chromium, it can be cooled unchanged from the range of stability to the range of persistence. As a progressive increase in the content of such elements depresses the lower limit of the range of stability, raises the upper limit of the range of persistence, and diminishes the rate at which the austenite can decompose in the intervening range, it follows that as the content of such elements increases it becomes easier to cool austenite to the range of persistence. In fact, when sufficient amounts are present the difficulty is to get the austenite to decompose, and when this difficulty exceeds a certain limit the range

of stability and persistence have to be regarded as merged so that it is impossible to discover where one begins and the other ends.

Having outlined the effects of heating and cooling operations on metals that are solidified under conditions that depart from equilibrium or undergo transformations in the solid state, it remains to refer briefly to the effects of such operations on metals rendered unstable by working. This aspect is more fully discussed in Chapter IV, particularly in the sections dealing respectively with Heating after Deformation, and Recrystallization. It is there shown that when a metal is mechanically deformed certain changes in the crystal are produced. As a result of these the metal is strain-hardened and the crystals are rendered unstable. A tendency for the metal to revert to a stable condition by the process of recrystallization is thus created, and when this tendency has an opportunity to come into operation the deformed crystals are replaced by new ones and strain-hardening is eliminated. Under certain conditions, and particularly in the case of steel, recrystallization after deformation is preceded by a phenomenon known as strain-ageing which leads to an increase in hardness over and above that which accompanies deformation. Furthermore, in certain metals, and under certain conditions, strain-hardening may be partially eliminated before recrystallization begins. In general, therefore, when all the relations between deformation, time, and temperature are considered in connexion with different metals very complicated conditions arise as shown in Chapter IV. For the present purpose, however, attention may be confined to metals that do not recrystallize at or near atmospheric temperature, and which are severely deformed in the cold, then heated to temperatures at which recrystallization occurs rapidly and at which ageing is not important. Under these conditions the main effect of heating is to produce recrystallization and eliminate strain-hardening, but the average size of the new generation of crystals increases progressively with the heating temperature and to a less extent with the time of heating.

All the effects of heat treatment mentioned in this section are not necessarily the specific objects of definite heat-treating operations, but as heating may have so many effects it usually happens that an operation carried out for one purpose produces one or more other changes. Thus during heating for working the heterogeneity in solid solution crystals may be wholly or partly eliminated. In heating aluminium alloys for solution treatment, spheroidization of undissolved constituents may occur, in annealing steel to eliminate work-hardening or machining stresses, spheroidization of pearlite may occur, and in heating other metals to eliminate work-hardening some age-hardening change may be promoted.

The Annealing of Castings.

We have now dealt with most of the general features of thermal and mechanical operations, viz. with (1) internal stress, (2) the effects of the

time and temperature of heating and the rates of heating and cooling, (3) furnace atmospheres, and (4) the general structural and constitutional effects of heating operations. It is now possible to consider the operations involved in thermal and mechanical treatment in the order in which they are performed.

Metal castings are subject to various defects, including gas and contraction cavities, hot-tears, and surface imperfections. None of these are affected by heat treatment, and when this is carried out it is with the object of eliminating internal stress or producing constitutional and structural changes. Castings of heat-treatable metals such as steel, cast iron, and aluminium alloys may be subjected to any of the thermal operations used in modifying the properties of such alloys, e.g. steel or iron castings may be hardened and tempered and aluminium alloy castings may be solution-treated and age-hardened. The annealing of cast metals, is, however, a specific operation involving slow heating and cooling, and carried out with the general object of eliminating internal stress. In the case of steel the operation is also used to bring about an improvement in the microstructure.

Castings in non-ferrous metals are rarely annealed. Owing to their ductility the internal stress produced by cooling is not of serious magnitude, and although in certain alloys some improvement in properties may be obtained by promoting constitutional and structural changes, the advantages obtained in this way are not in general sufficient to make annealing worth while. Iron castings are annealed to remove internal stress, and when this is the only purpose of the treatment it is performed between 420° and 520° C. in order to prevent cementite changing to graphite. When, however, the object of the annealing is to soften the metal for machining, the change from cementite to graphite is promoted by heating between 760° and 820° C. One method of obtaining grey cast irons with a fine structure is to cast a white or mottled iron (i.e. with most of the carbon as cementite) and anneal at about 930° C. to promote the formation of graphite. In this way very strong, machinable irons are obtained. Finally, the prolonged annealing of white-iron castings leads to the production of malleable cast iron. This operation is a process of manufacture rather than a treatment and will be further considered in Chapter XIV.

Steel castings are heat-treated to eliminate internal stress and to improve the structure. In the cast metal the austenite grains are large and there is a considerable variation in composition between different parts of each grain as a result of selective crystallization. During cooling a coarse ferrite-pearlite structure is produced. To secure the greatest improvement in structure it is necessary to remove the heterogeneity as far as possible and to obtain a fine ferrite-pearlite structure. For the former purpose heating to a high temperature is desirable, for the latter, heating just above the critical range followed by air cooling is best, while for the removal of stress slow cooling is necessary. Various treat-

ments are therefore performed on steel castings in order to obtain such improvements as circumstances permit. With this object in view they may be full annealed, normalized, normalized and annealed, or double annealed.

Full annealing consists of heating above the critical range, maintaining there for a suitable period of time and cooling slowly. Normalizing is similar except for the fact that the castings are cooled in air. Either of these treatments may be carried out at about 50°C . above the critical range, i.e. at 940°C ., if the steel contains 0.1 per cent. of carbon, and at 840°C . if it contains 0.6 per cent. This temperature is a compromise between the high temperatures necessary for promoting homogeneity and those suitable for obtaining the smallest austenite grains. When better results are required two treatments may be performed, a homogeneizing treatment at a high temperature, i.e. about 950°C . to $1,000^{\circ}\text{C}$., and a refining treatment at the same temperature as would be used for normalizing a forging of similar composition, i.e. 920°C . for 0.1 per cent. of carbon and 820°C . for 0.6 per cent. of carbon. This is double annealing if cooling is carried out in the furnace and double-normalizing if it is carried out in air. Normalizing has the advantage that it produces a finer ferrite-pearlite structure from austenite grains of a given size, but it is not suitable for the elimination of internal stress. When it is adopted, therefore, it should be followed by low temperature annealing below the critical range. The very best results for the heat treatment of a steel casting should be obtained by a full anneal at a high temperature to produce homogeneity, normalizing just above the critical range, and a final annealing below the critical range. In practice, however, a full annealing treatment is usually considered sufficient.

Heating for Hot-working.

The primary object of the heat treatment that precedes or is performed at intermediate stages in hot-working is to raise the metal to the temperature at which it becomes plastic enough for such working. The operation is essentially simple, but it has to be carried out on many different kinds of metal in masses of varying size and shape, and numerous precautions must be taken if the best results are to be obtained. Steel ingots are generally removed from the mould and transferred to a 'soaking-pit' while they are still at the forging temperature. This procedure is indispensable when the ingots are large or consist of hard steel, but those of small dimensions and of metals other than high carbon or alloy steel may be allowed to cool with safety and re-heated to the forging temperature as required. At certain stages during hot-working the articles require to be re-heated in furnaces specially designed for handling such stock as billets, slabs, plates, rods, and other products of the hammer, rolls, or forging press. The number of times that a given article must be so re-heated depends not only on the amount of work required to produce the final shape, but also on the equipment

of the mill, and one which is designed for rapid work may perform without reheating a series of operations that require several reheatings in a less efficient plant. Reheating operations differ from each other with respect to the metal, its shape and size, and the type of furnace in which it is treated, and much could be written about them. For the present purpose, however, attention may be confined to such general aspects of the process as temperature, rate of heating, uniformity of heating, and furnace atmospheres.

Working is facilitated by heating to the highest possible temperature, but in every case if a certain limit is exceeded there is danger of overheating or burning and the rate of formation of scale is greatly increased. For each particular metal the most suitable temperature for heating in preparation for working is therefore fairly definitely fixed as the highest to which it may be heated without reaching the above limit. This applies more particularly to the stiffer alloys such as the steels, nickel alloys, strong aluminium alloys, and brass, for there is not the same need to heat soft metals like copper and aluminium to the highest permissible temperatures. In general, steels are heated to the range $1,100^{\circ}$ to $1,350^{\circ}$ C., nickel and its alloys to $1,100^{\circ}$ to $1,200^{\circ}$ C., copper alloys to about 800° C., and aluminium alloys to about 450° C. The highest temperature to which steel may be safely heated decreases as the carbon content increases, and is further decreased by the addition of alloying elements. A temperature about 200° C. below the solidus is usually accepted as the highest permissible in heating carbon steels, whereas the alloy steels, which generally contain from 0.1 to 0.3 per cent. of carbon should be heated at temperatures about 50° to 70° C. below those used for carbon steels of the same carbon content. At any given temperature they are stiffer than carbon steels and consequently there is more danger of their being overheated in endeavouring to obtain greater plasticity.

To achieve the best results the stock must be uniformly heated throughout to the correct working temperature. The furnace accordingly should be designed and the stock packed so that heat has access to the whole of its surface, and the metal should be kept in the furnace until the necessary temperature has been reached at the centre of the heaviest sections. When ingots or large billets are being heated, a considerable time is required for the metal to become uniformly heated to the temperature of the furnace. This is frequently done during the first heating of steel ingots in order to permit diffusion to take place, but leads to the formation of a large amount of oxide. It is common practice in certain re-heating operations to maintain the furnace at a temperature about 150° C. higher than that to which the metal should be heated and so reduce the time of heating. In this case a temperature gradient is produced in the metal undergoing treatment. So long as this is not too pronounced it does not lead to any difficulties during subsequent forging, but there is a tendency to accelerate the heating operation by

maintaining the furnace at a temperature very much in excess of that required in the metal, and as a result a great difference in temperature is set up between the outside and inside of the pieces treated. This is not conducive to good forging practice.

Mild steel, and the ductile non-ferrous metals may be heated fairly rapidly without danger of cracking, but when medium carbon, high carbon, or alloy steels are being heated the temperature must not be allowed to rise too quickly or cracks will form. For this reason these alloys should not be charged directly into a furnace held at the forging temperature but should either be pre-heated or charged into a cold furnace and heated up with it. Continuous furnaces are very suitable for slow heating, for as the stock moves towards the hot zone it is gradually heated by the spent gases which flow in the opposite direction and give up their heat to it. When batch furnaces are used pre-heating must be carried out in a separate furnace and the stock then transferred to the furnace at forging heat. As cracking due to thermal stress takes place at comparatively low temperatures rapid heating may safely be employed once the metal has been pre-heated to 700° C. The safe rate of heating to this temperature varies with the properties of the steel and the mass of the piece, but in general about 30 minutes per inch of thickness should be allowed for all steel except mild steel.

HOT-WORKING

Hot-working is the mechanical shaping of metal in a range of temperature in which no increase in hardness is produced by deformation, and is thus distinguished from cold-working which is performed in a range of temperature in which the metal becomes harder as deformation proceeds. The increase in hardness produced by cold-working sets a limit to the extent to which the shape may be changed, and when this has been reached the metal must be restored to its soft condition by annealing before further work can be done. There is no such limit to the extent to which the shape may be changed by hot-working, but as the common metals with the exception of lead, tin, and zinc have to be heated to obtain the required plasticity, the amount of work that can be done without re-heating is limited by the time taken to cool to a temperature at which the metal becomes too stiff for easy deformation.

If the hot-working of a metal resulted only in a change of shape, it would be a much less common operation than it now is, and many articles produced in this way would be made by casting, which is generally cheaper. As a result, however, of the improvement in mechanical properties which is always obtained by working, this method of shaping is used whenever possible in the manufacture of parts requiring good mechanical properties, and casting is only employed when cheapness is the first consideration or when the required shape cannot be produced by working. This improvement in properties

results from (1) a general consolidation of the metal and closing of gas and contraction cavities by means of mechanical pressure, (2) a refinement of the crystal structure, and (3) a destruction of the continuity of intergranular concentrations of impurities and inclusions. These effects of hot-working on cast metals will be described in greater detail in a subsequent section.

Methods of Hot-working.

The detailed procedure involved in the mechanical shaping of the innumerable articles produced in this way is a subject of infinite complexity, but the general methods may be described fairly briefly if details are omitted. The greatest tonnage of worked metal is produced by rolling, but forging under the hammer or the press is widely employed, and extrusion is used extensively in shaping some of the softer metals. Each method has its particular advantages and disadvantages from the point of view of cost, effect on the metal, shapes to be produced, and masses to be handled. Generally, however, shape, size, and properties determine the method of working used, and articles of simple shapes such as plates, sheets, bars, rods, rails, and angles are rolled; more complicated shapes of small or medium size, such as crankshafts, automobile axles, and numerous small parts are made under the hammer; heavy forgings such as guns, armour plates, and pressure vessels are shaped in a press; and tubes, rods, and various sections of brass and other plastic metals are made by extrusion. Frequently, two methods of shaping are used in the manufacture of one article, and ingots from which drop forgings have to be made are usually rolled down to bars of a size suitable for forging into the shapes required.

Rolling.

The rolls used for shaping metals are made of steel or cast iron. When the latter alloy is used it is cast so that the outside is chilled and consists of white iron. This surface is very hard and can be made smooth by machining. Such rolls are very suitable for finishing, but because of their brittleness are not so satisfactory for the heavier work required in the earlier stages of rolling. In the roughing rolls strength rather than hardness or smoothness is required, and steel containing between 0.5 and 0.75 per cent. of carbon is usually preferred to cast iron. In order that the rolls may grip the piece they must be made of such a diameter that the upper and lower edges of the entering piece meet the circumferences of the rolls at points not more than 30° from the plane containing the axes of the rolls. Thus their diameter is to some extent determined by the thickness of the stock being rolled. To facilitate gripping, the surfaces of the rolls, except the finishing rolls, are ragged. On those in which the ingot is first reduced these indentations are very large, like the cogs on a cog-wheel, and such rolls are known as the 'cogging rolls'.

The rolls used for plates, sheets, and simple rectangular sections are frequently plain cylinders like those in the mill shown in Fig. 241. During rolling, however, there is a certain amount of expansion sideways and this is liable to produce bulging sides and uneven edges. To prevent this rolls are made with 'collars' at suitable distances. Another method of achieving it is by the use of a 'Universal Mill' which has a

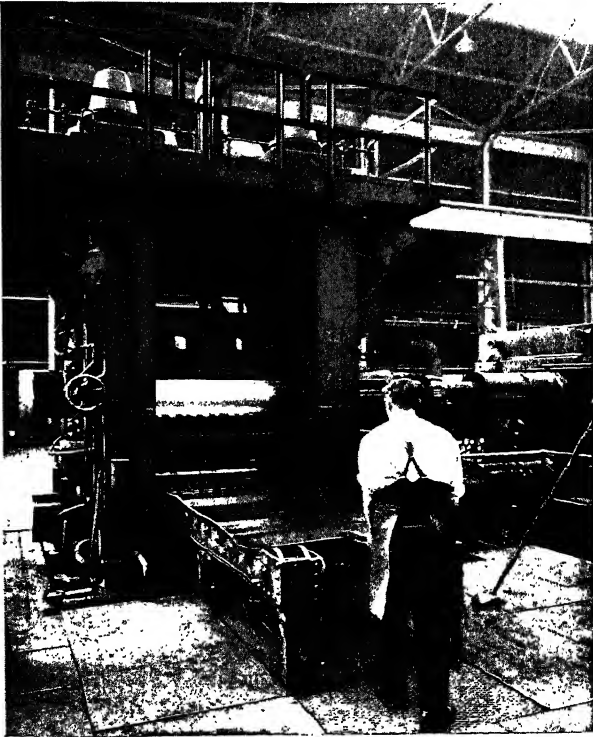


FIG. 241. Hot-rolling sheet mill.
(Henry Wiggin & Co. Ltd.)

pair of auxiliary vertical rolls between which the piece passes on, emerging from the horizontal rolls. As the distance between the vertical rolls can be set at any desired width such a mill can be used for a variety of sizes without changing the rolls as is necessary when rolls with collars are used. In the rolls used for small square sections wedge-shaped grooves are cut and the combination of the wedges in the upper and lower roll gives what is called the diamond pass. For other shapes appropriate grooves are cut like those in the rolls in Figs. 242-4.

Only a limited amount of reduction can be produced in each pass through the rolls, and consequently the shaping of metals by rolling entails many passes. The most expeditious working is obtained when a separate pair of rolls is available for each pass. The metal then moves

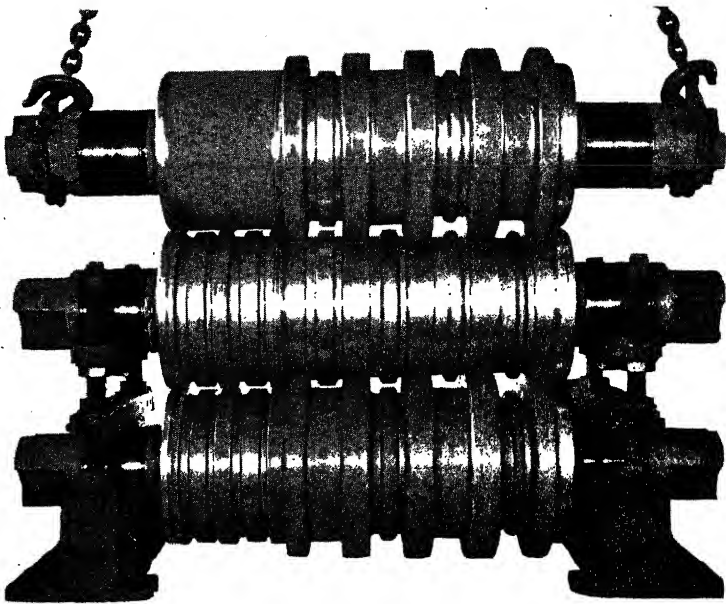


FIG. 242. Set of three-high bull-head rail rolls.
(C. Arkell & Co. Ltd.)

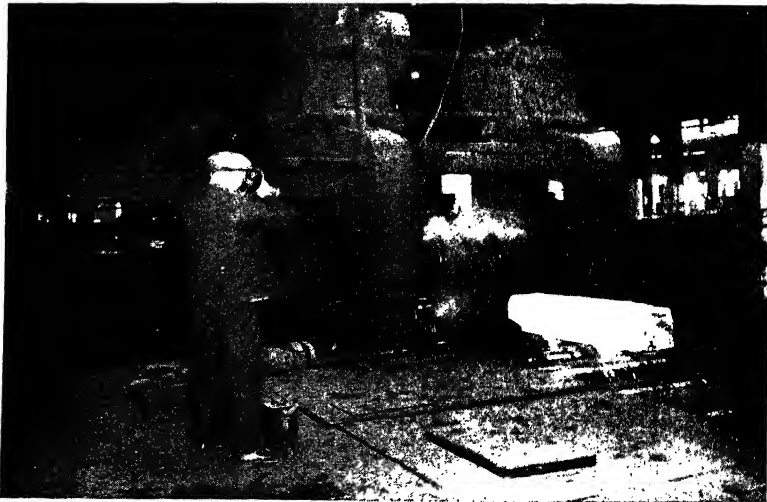


FIG. 243. Cogging an ingot.
(The United Steel Companies, Ltd.)

continuously in one direction and all the rolls run without interruption. Such equipment is only possible, however, when there is an outlet for a very large production of a certain kind of article. The installation of the necessary plant requires a large capital outlay and regular and rapid production is necessary for economic success. This applies particularly to the steel industry in which heavy plant is required and continuous mills are therefore less common than in the non-ferrous industries. As plant of this kind is the exception rather than the rule, methods of



FIG. 244. Finishing 6 in. 'rounds'.

(Thos. Firth and John Brown, Ltd.)

operation have to be employed that permit successive passes through the same pair of rolls. With a stand consisting of two rolls running continuously in one direction successive passes can be obtained by returning the piece to the entrance side over the top of the rolls. This is known as a 'Return' or 'Pull-over' mill, and obviously it can only be used when the stock being rolled is fairly easy to handle. The method is now used mainly in rolling light sheet for tin-plate and similar purposes, the distance between the rolls being adjusted between each pass. The most widely used type of mill is known as the 'Three-High Mill'. In this there are three rolls and the metal passes in one direction between the middle and bottom rolls and in the other direction between the middle and top rolls. By the use of suitable mechanism for handling the stock, fairly heavy articles can be rolled in three-high mills, but for the heaviest work 'Reversing Mills' are employed. These are used very widely for the preliminary rolling of steel ingots. After each pass the engine is reversed, the rolls readjusted, and the ingot passed through in the opposite direction.

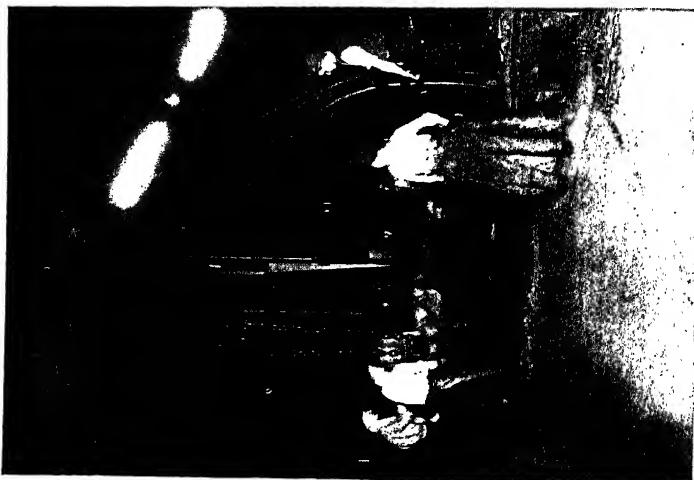


FIG. 245. Forging hammer.
(Thos. Firth and John Brown, Ltd.)

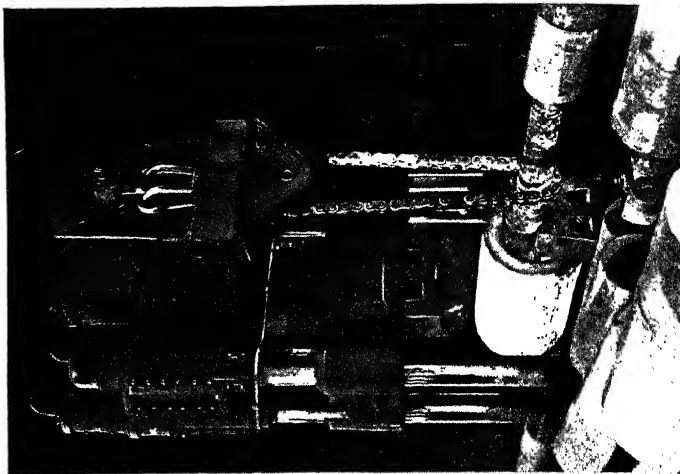


FIG. 246. Forging press.
(Thos. Firth and John Brown, Ltd.)

In the non-ferrous industry ingots are generally made of such a size that they can be rolled down as a whole to the final form required. This is not the general practice in the steel industry, except when large articles are being made. Usually, the ingot is of such a size that a number of the finished articles can be made from it, and the first stage in rolling is to reduce the ingot to such dimensions that it can be cut up into suitable portions and the top part containing the pipe discarded. In this way billets, blooms, and slabs are produced, and these after reheating are rolled in suitable mills into rails, tyres, sections, angles, joists, plates, bars, rods, and strip. From the bars thus produced thin sheets are made by further rolling, and bars of suitable sizes also constitute the raw material of the light-forging industry. From the small rods produced by hot-rolling, wire is made by cold drawing, and from the strip, welded tubes are manufactured.

Forging.

Forging may in the first instance be said to be carried out by means of a hammer (Fig. 245) or a press (Fig. 246). Hammers are steam-driven and the blow delivered is rapid. Because of this the effect of the mechanical pressure does not penetrate throughout heavy sections, and hammers are therefore used for lighter work than the hydraulic presses which exert a slow, steady pressure. For heavy press forgings such as gun tubes, large crankshafts, boiler drums, and pressure vessels, a complete ingot from which the top and bottom portions have been removed is used, for lighter articles the ingot is rolled down to a billet and suitable lengths cut off for working under the hammer. Forming is carried out by means of tools of comparatively simple shape attached to the anvil and hammer or ram or held between them, as shown in Fig. 247. By manipulating the metal the requisite changes in shape are produced in much the same way as by a blacksmith. When hollow forgings are being made the centre of the ingot is trepanned out cold, or punched out hot, and forging is then performed on a mandril as shown in Fig. 246. In this illustration the long axis of the top tool is parallel to the axis of the drum and the operation shown is designed to increase the diameter and decrease the wall thickness. By using a tool with the long axis at right angles to this, the length of the drum may be increased as shown in Fig. 248. Some of the steps involved in making

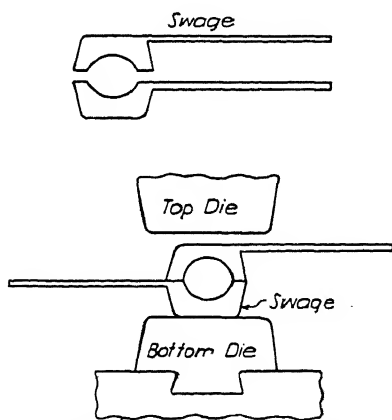


FIG. 247. Swages used in hammer forging.

(*Transactions of the American Society for Metals*, 1937 (Steever).)

manipulating the metal the requisite changes in shape are produced in much the same way as by a blacksmith. When hollow forgings are being made the centre of the ingot is trepanned out cold, or punched out hot, and forging is then performed on a mandril as shown in Fig. 246. In this illustration the long axis of the top tool is parallel to the axis of the drum and the operation shown is designed to increase the diameter and decrease the wall thickness. By using a tool with the long axis at right angles to this, the length of the drum may be increased as shown in Fig. 248. Some of the steps involved in making

a forged-steel boiler drum are shown in Fig. 249 and may be described as follows: The ingot *A* is withdrawn from the mould while hot and transferred to an annealing furnace. When it has become uniform in temperature it is cooled slowly in the furnace, the top and bottom ends are then parted off in the machine shop and the core removed by trepanning (*B*). The hollow bloom is then heated to about $1,200^{\circ}\text{C}$. and opened out to the required dimensions as shown at *C*. The opened-out bloom is then reheated and forged as shown at *D*. Heating and forging are con-

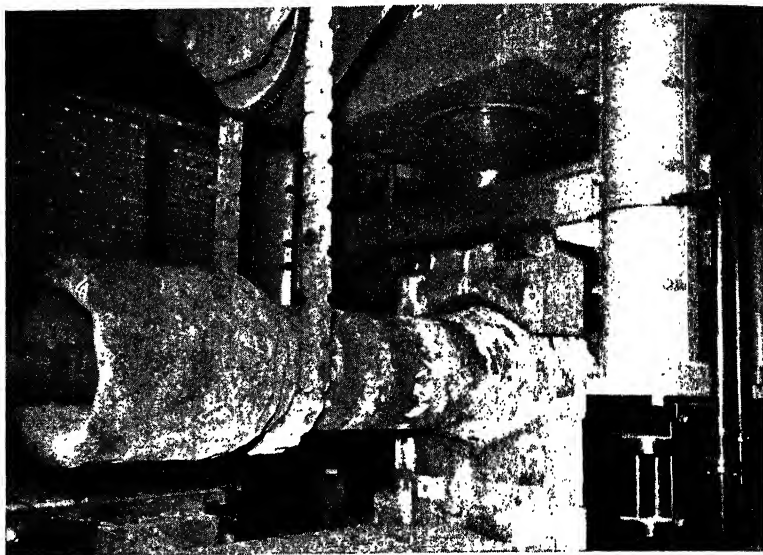


Fig. 248. Forging drum for high-pressure boiler.
(The English Steel Corporation, Ltd.)

tinued until the tube is complete as shown at *E*. After this the tube is normalized, rough-machined on the outside, and bored inside. The ends are then heated and closed by using special tools and careful manipulation. Finally, the forging is again normalized and finish-machined.

Forging operations of the type just described are practically confined to the manufacture of comparatively heavy articles in steel. The shaping depends to a large extent on manipulation of the stock; tools must be changed from time to time, and in general the process is expensive and only justified when large articles are being made, when the very best properties are required, or when no large-scale production of identical parts is involved. When, however, smaller articles are being made in numbers, one of the processes of forging between specially prepared dies is used. Such processes are again used mainly in shaping steel, but are also employed extensively in forging aluminium alloys, and, to a less extent, $\alpha+\beta$ brass. The most widely employed of these is drop-forging. For shaping by this method the metal is first rolled into

a bar of suitable size. From this the article required is forged by striking the heated metal between matched dies attached to the anvil and hammer of the machine. The hammer most commonly used is the board hammer which is raised mechanically and dropped from a suitable

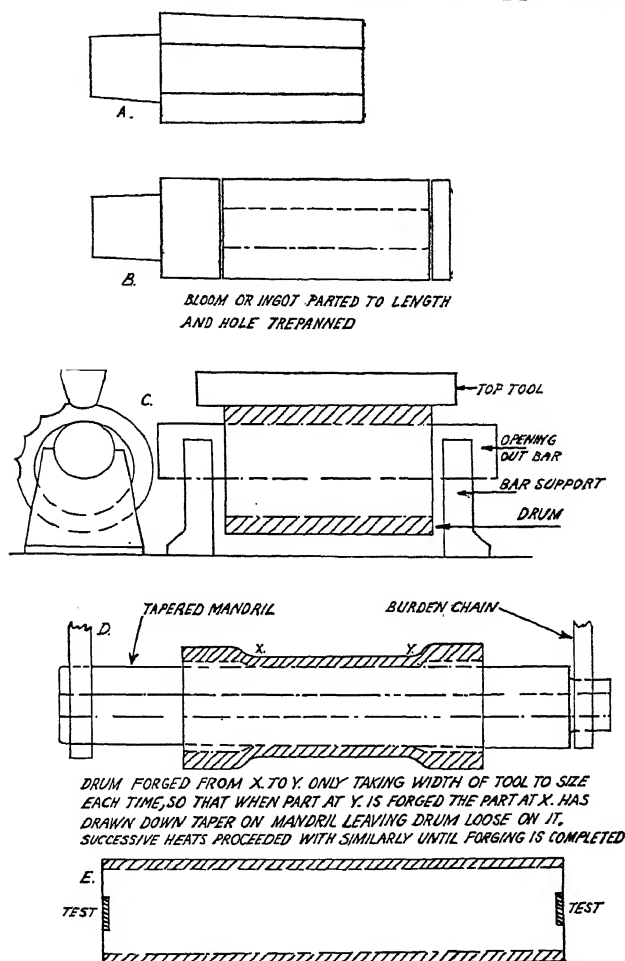


FIG. 249. Stages in manufacture of forged steel boiler drum.

(*Metal Treatment.*)

height, but steam hammers in which steam pressure acts during the down-stroke are also used. The dies may be made from heat-treated carbon steel containing from 0.5 to 0.9 per cent. of carbon, but alloy steels containing chromium, and various combinations of nickel, molybdenum, vanadium, and tungsten are widely used.

A typical die contains several features known as the fuller, edger, blocker, finishing-impression, and cut-off. The object of the fuller,

edger, and blocker impressions is to transform a suitable length of bar into a form that roughly resembles the finished article, then the final shape is produced in the finishing-impression. Figs. 250 to 252 illustrate various stages in drop-forging a connecting-rod. In Fig. 250 the bar is being shaped in the fuller where by moving and turning it as the hammer strikes the first stage in forming is carried out. The next stage is performed in the edger (Fig. 251), where again several blows are struck by the hammer, and finally the roughly shaped connecting-rod is driven into the finishing-impression by a series of blows of increasing strength (Fig. 252). The forging is then parted from the bar with the cut-off, and the flash produced by metal being forced between the two halves of the finishing-impression (Fig. 252) is removed in a trimming punch. This last operation may be carried out hot in a press adjacent to the drop-hammer as shown in Fig. 253. Here the connecting-rod is placed on a trimming die and the top die descends and forces it through the trimming die which shears off the flash. Alternatively, trimming may be carried out cold. Numerous components are made by drop-forging, among which may be mentioned steel and aluminium alloy connecting-rods, automobile axles, crankshafts, and gear blanks. Sometimes, as in the manufacture of a crankshaft, several pairs of dies are required.

Hot-pressing between dies is an operation that resembles drop-forging except that shaping is carried out by means of steady pressure instead of by blows. The press, however, is not as flexible as the stamp and is not so suitable for shaping components from bar stocks unless these are of very simple shape. It is, however, very suitable for producing accurate final dimensions, and components previously shaped by drop-forging are sometimes pressed between dies in order to obviate the need for subsequent rough machining. In the case of steel this may be done at the normalizing temperature. In the case of aluminium alloys it may be done cold. Another operation that involves shaping between dies is that known as upset or machine forging. This machine is a horizontal press and is used exclusively for operations that require expanding or increasing the diameter of the bar stock supplied. Thus it is employed for the manufacture of rivets, bolts, gear-blanks, rings for ball-bearings, automobile axle-shafts, drag links, &c. Bars are heated over part of their length and fed into the machine which makes the forgings and parts them off until the heated length is used up. A recent application of this type of machine is in the manufacture of aero-engine cylinders from bar by upsetting and expanding.

Extrusion.

By the process of extrusion, rods, tubes, and all kinds of sections are made by forcing hot solid metal through dies of appropriate shape. A diagrammatic sketch of an extrusion press is given in Fig. 254. The metal to be extruded is placed in the container and forced out through the die by means of the hydraulically driven ram, and in this way a



FIG. 250. Drop-forging.
(*Metal Progress.*)

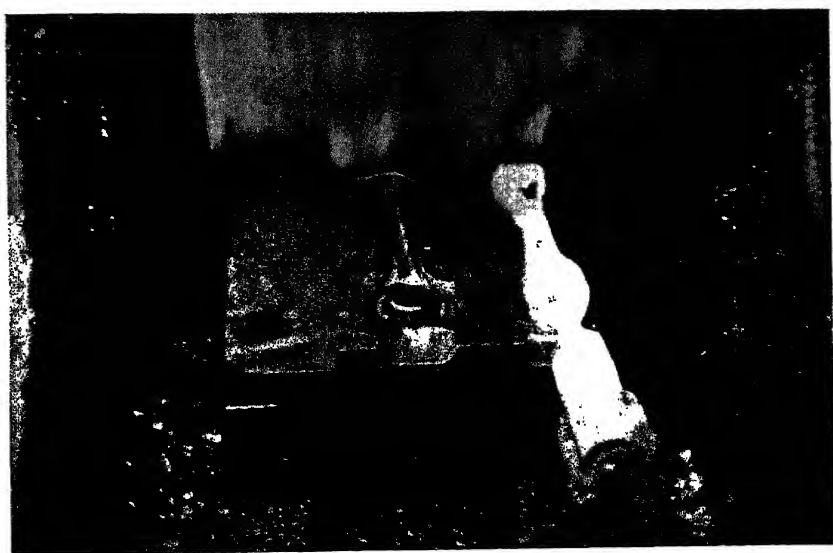


FIG. 251. Drop-forging.
(*Metal Progress.*)



. 252. Drop-forging. The Finishing-impression.
(*Metal Progress.*)



FIG. 253. Drop-forging. Trimming.
(*Metal Progress.*)

circular, square, hexagonal, or any other shape of rod as well as all kinds of simple and complicated sections can be obtained. When tubes are required the centre of the die orifice has to be closed by a mandril so that the metal is compelled to flow through an annular space. One way of doing this is to pierce the metal billet before putting it into the container. The mandril, which passes through the ram is then moved into position in the die and the ram set in motion to force the metal between

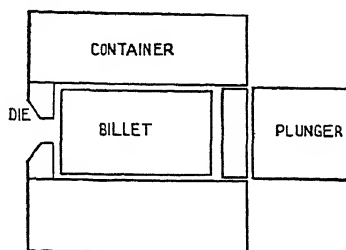


FIG. 254. Extrusion press.

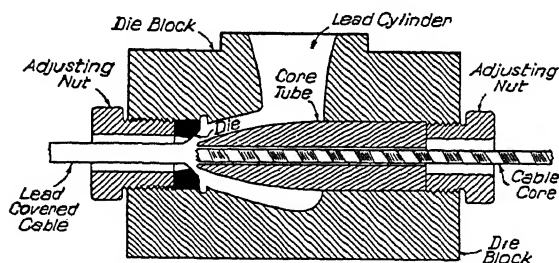


FIG. 255. Die-block assembly used in extruding lead cable sheath.

(*Transactions of the American Society for Metals*, 1937.)

the mandril and die. Alternatively, a solid billet may be placed in the container and pierced with the mandril, or, as in the extrusion of lead pipe, molten metal may be run into the container while the mandril is in position.

Extrusion is used for the manufacture of rods, tubes, and sections in numerous non-ferrous metals, i.e. lead, tin, copper, aluminium, magnesium, and their alloys. In the manufacture of lead pipe the metal is run molten into the container and extruded when it has solidified and cooled to about 220°C . The sheathing of lead cable is a similar operation to the manufacture of pipe and a section through the die-block assembly is shown in Fig. 255. The molten lead is cast in the cylinder above the die-block, and when forced downwards by the ram (not shown) the lead is squeezed out through the die as a sheath on the cable core. In extruding copper-base alloys hot billets are charged into the container. The alloy most widely used is 60:40 brass or variants of this such as free-cutting brass (61.5 per cent. copper, 35 per cent. zinc, and

3.5 per cent. lead) or forging brass (60 per cent. copper, 38.25 per cent. zinc, and 1.75 per cent. lead), but numerous other alloys, e.g. naval brass, manganese bronze, nickel-silver, aluminium bronze, and pure copper, are also extruded. From the extruded products, rivets, screws, hinges, lock bodies, valve stems, pinions, gears, and numerous other articles are made by forging or machining; tubes are used in condensers, distillers, and heat-exchangers, and sections are used for various purposes including architectural fittings. Aluminium and its alloys are also extruded in a variety of forms for numerous ultimate uses, the alloys most widely employed being commercial aluminium, aluminium-manganese, aluminium-silicon-magnesium, and aluminium-copper-silicon-magnesium alloys. Extrusion is also applied extensively in the shaping of magnesium and tin-base alloys, but less frequently in the case of zinc and its alloys. There has been no real commercial development in the extrusion of metals with a higher melting-point than copper, i.e. alloys based on iron or nickel, for it is difficult to get dies to withstand the high temperature necessary. According to Crampton (275), however, one plant is at present extruding stainless-steel tubing in commercial quantities and another is extruding nickel, Monel metal, and similar alloys.

Tube-making.

Extrusion provides a convenient method of making tubes. It is used exclusively in the manufacture of lead tubing and, to a large extent, in that of aluminium and copper-base tubing. For these latter, however, other methods are also used, and for steel and nickel alloys different methods are employed. These may now be described briefly with particular reference to steel.

Tube-making processes other than extrusion may be divided into two types: (a) welding processes, and (b) seamless processes. Butt-welding is suitable for making tubes from $\frac{1}{8}$ in. to 3 in. diameter from steel containing not more than about 0.15 per cent. of carbon. The metal is rolled into lengths of strip (skelp), a point is made at one end of each length, and the skelp is heated to a welding temperature ($1,450^{\circ}\text{C.}$). It is then drawn from the furnace through a bell so designed that the skelp is gradually curled up to form a complete circle with the edges abutting. The edges, thus pressed together at a high temperature, weld, and a tube is produced. This tube is then reduced slightly in diameter by rolling without a mandril and finally straightened in straightening rolls. A stronger type of weld is produced by lap-welding. In this process the skelp is heated to $700\text{--}800^{\circ}\text{C.}$ and pulled out of the furnace through scarfing rolls which taper the edges, then through a bell which curls the skelp into a circle with edges overlapping. This tube is next heated to $1,450^{\circ}\text{C.}$ and passed through a pair of grooved rolls over a mandril. In this operation the mandril supports the tube on the inside while the rolls weld the overlapping edges. The tube is then sized and

straightened. Lap-welding is suitable for the production of tubes from $1\frac{1}{4}$ to 30 in. diameter, from steel containing not more than 0.15 per cent. of carbon. Hammer-welding is used for making larger tubes, up to 96 in. in diameter. The strip is heated and scarfed as for lap-welding and is then bent in a stand of three rolls so arranged that the strip is curled round the top roll. The tube thus formed is drawn off from the end of this roll and passed through the welding machine which heats the overlapping edges and welds them by hammering. Another type of butt-welded tube is made by resistance-welding. Skelp is bent cold into the form of a tube with edges abutting. It then goes to the welding plant in which the edges are kept pressed together by rolls while a heavy current passing between a pair of copper discs that straddle the seam heats this to welding temperature. This process is said to be capable of welding steel containing up to 0.3 per cent. of carbon.

The first method of making seamless tubes was introduced by Mannesmann in 1897, and since then the demand for tubes of high strength for withstanding pressure and for structural purposes has promoted the rapid development of this type of process. Seamless tubes are made by piercing a hole in a circular billet heated to 1,250–1,350° C., and Mannesmann's invention was a method of doing this by rotary piercing. The basic principle of the process is that when a solid circular billet of plastic metal is subjected to compression on one side, tensile stress in a direction at right angles to this is developed at the centre. This tends to rupture the metal there, and if the billet is rotated so that the direction of compression moves round a circle then a circular cavity will tend to form. The object of the Mannesmann rolls is to subject the billet to transverse compression while rotating it, and at the same time to force it forward over a pointed mandril. The rolls used are shown in Fig. 256. Each roll is about 30 to 40 in. in diameter in the middle where there is a flat about 1 in. wide, and from this the rolls taper towards each end at an angle of from 5° to 10°. When set in the machine they lie side by side instead of above each other, but their axes are not parallel. Viewed from above as in Fig. 256 they are inclined in opposite directions each making an angle of from 6° to 12° with the line of advance of the billet. Viewed from the side the axes are again inclined in opposite

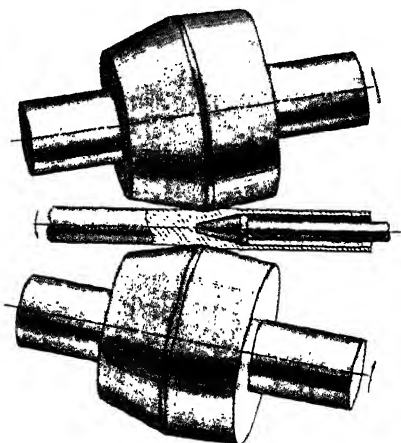


FIG. 256. Rolls used in Mannesmann process for piercing billets.

(*American Society for Metals*, 1931.)

directions so that they cross at the middle of the rolls. A round billet of suitable size is centred on one end to the depth of about 1 in., and then heated to the rolling temperature. A mandril with a pointed nose is attached to a water-cooled rod and inserted between the rolls so that its point just passes the line where the rolls cross. When the heated billet is pushed between the rolls it is gripped, revolved rapidly, and drawn slowly forward. The forces acting on the plastic metal are such that the centre is opened out and the billet forced over the mandril,

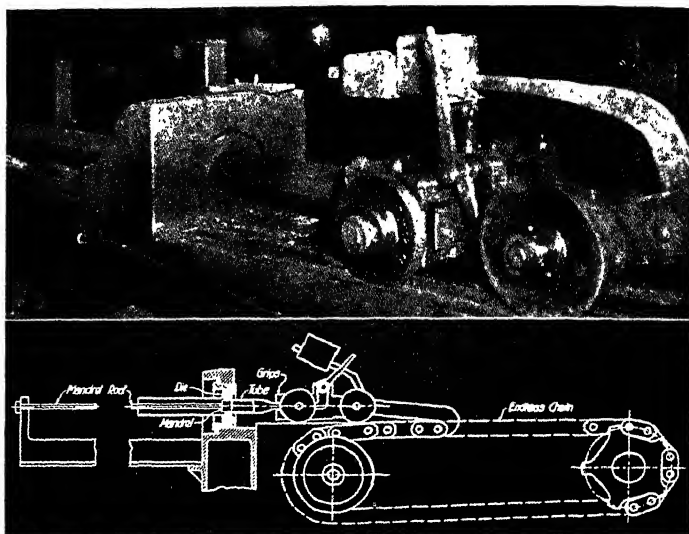
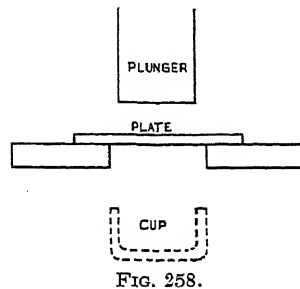


FIG. 257. Method of drawing tubes.
(*American Society for Metals, 1931.*)

which together with its supporting rod, revolves in a thrust bearing at the same rate as the billet. When the billet emerges from the mill it is in the form of a thick-walled tube of fairly uniform thickness. In the Stiefel machine the same result is obtained by rolling between discs.

After the piercing operation the short thick-walled tube is rolled over a mandril between grooved rolls. Several passes are given, and in this way the tube is elongated, the wall thickness diminished, and the approximate outside diameter produced. It then passes to the reeler, which, like the piercing mill, is a machine designed to roll obliquely. A mandril is again used and the outer and inner surfaces of the tube are burnished and a good surface thus produced. The tube is now of the correct wall thickness but its diameter is greater than that required. The final operation consists of rolling to the correct size. If the product of the earlier operations is only slightly above size the final rolling is done in one or two passes, but if its diameter has to be greatly decreased it is passed through a sinking mill which may consist of as many as sixteen or more pairs of grooved rolls.

Rotary piercing processes such as the Mannesmann and Stiefel are suitable for making seamless tubes from good quality carbon and alloy steels of numerous varieties, and they are also used extensively in the manufacture of non-ferrous tubes. The largest size that can be made is about 9 in. diameter and the smallest size that can be finished hot is about $1\frac{1}{2}$ in. diameter. Smaller sizes may, however, be made by subsequently cold-drawing hot-rolled tubes, and this operation may also be performed on the larger sizes when the superior surface, greater strength, and thinner wall thicknesses obtainable by cold drawing are required. Although this is a cold-working operation it may be described here in order to complete this brief account of the manufacture of seamless tubes. For this operation one end of the hot-finished tube is pointed by swaging, i.e. hammering between semi-circular dies. It is then pickled, washed, and water-coated, as described later in connexion with the manufacture of wire, and drawn over a mandril and through a die. The arrangement for drawing is shown in Fig. 257. The pointed end of the tube is passed through the die and gripped by the shackle on the carriage. The mandril is adjusted so that it lies inside the tube just where it passes through the die and thus controls the internal diameter. The carriage is then attached to the endless chain and the tube drawn through. Only a small reduction can be accomplished in each pass, and with steel, annealing has to be performed after each pass, and unless this is done in a non-oxidizing atmosphere it must be followed by pickling. Inter-pass annealing is carried out at $700^{\circ}\text{C}.$, and after the last pass the tubes may be again annealed or put into service in the cold-worked condition.



Seamless tubes and cylinders in steel and non-ferrous metals can also be made by the cupping process. A disc is punched out hot from a sheet and pushed through a hole in a die by means of a ram as illustrated diagrammatically in Fig. 258. The cup is then reheated and pressed through a smaller hole to produce a deeper and narrower cup which after again reheating is pushed by one ram through a series of dies (3 to 12) to form a long cylinder. In the 'push-bench' process a square billet is placed in a circular container and a punch which forms a circular hole and expands the billet to fill the container is pressed into it. A short thick-walled cylinder closed at one end is thus produced, and it is then made into a tube by pushing through a series of dies.

Effects of Hot-working.

Besides providing a convenient way of producing a vast number of different shapes, hot-working has the effect of refining the structure of cast metals and eliminating many of their defects. It is evident that the

pressure applied during working will tend to close such cavities as are formed by the evolution of gas, the failure of the supply of liquid metal at the surfaces of growing crystals, and the differential contraction of parts of the metal after solidification is complete. This does not in itself result in a marked improvement in the properties of the metal, but if the surfaces of the cavities are not oxidized or otherwise contaminated, and if the metal is capable of autogeneous welding, then the walls of the cavities will weld together and the soundness of the metal be greatly improved. In the case of most of the common metals, e.g. aluminium, copper, nickel, and their alloys, cavities that are far enough below the surface not to be exposed to the atmosphere are largely eliminated during working. Moreover, the welding capacity of mild steel is so pronounced that satisfactory products can be thus obtained from very unsound ingots. But this does not hold to anything like the same extent for alloy steels and carbon steels containing more than 0.3 per cent. of carbon. To obtain sound forgings from them care must be taken to ensure that the original ingot is also sound.

Although hot-working tends to eliminate internal cavities it does not follow that all worked-metals are free from internal defects. Blowholes, e.g. when not satisfactorily welded, lead to hair-cracks in the finished articles. Similarly, internal cracks are liable to result from the concentrations of inclusions along the planes separating the groups of parallel columnar crystals, and those which divide the columnar from the equiaxed crystals. Such cracks do not appear on the surface of worked articles, but they are frequently revealed by machining.

Blowholes that are at or near the surface are not eliminated by working. Such blowholes may be due to gas evolved from improperly degasified metal when the casting conditions are not controlled so as to restrict the blowholes to the interior. Alternatively, they may be caused by casting in a mould with a badly oxidized surface. During the removal of the ingot from the mould, or in the initial stages of working, the thin skin of metal covering these holes may be broken, and as a result their surfaces are oxidized, and welding cannot take place. Subsequent working elongates and closes their sides without welding. They therefore appear in the finished work as long narrow cracks known as 'seams' or 'roaks'. Similar surface defects may arise from large inclusions located near the surface of the metal or from dirt adhering to the mould walls and picked up by the ingot. Whether originally covered by a thin skin of metal or not, these inclusions, or the places from which they have fallen through oxidation of the surrounding metal, are drawn out during rolling into elongated surface flaws. Surface defects are liable to be further extended during such operations as drop-forging, but their consequences are most serious when the metal is subsequently subjected to heat treatment involving rapid cooling. They can be largely removed at any stage by chipping out,

but in order to ensure their complete absence the ingots of high-quality steels and expensive non-ferrous metals are machined on the surface before rolling or forging.

Attention may now be given to the effect of working on the structure of cast metals, dealing in the first place with those which solidify as single phases, i.e. either primary solid solutions or malleable intermediate constituents like β in copper-zinc. Such metals are composed of varying assemblages of columnar and equiaxed grains. Throughout each grain the crystal structure is continuous (i.e. it is one crystal), but owing to the process of selective freezing that accompanies its growth there is a difference in composition between the primary skeleton and the matrix. Furthermore, although some of the inclusions are entrapped in the interstices of the grains they are mainly located at the boundaries between them, and finally, owing to the process of segregation, the average composition of the cast metal varies from region to region. It may be said in the first place that hot-working and the heating that accompanies it do not materially affect segregation, and if there is a concentration of impurities at the centre of an ingot this remains at the centre of anything made from it. Attention may thus be confined to the other three aspects of the cast structure, viz. (a) the crystal structure of the grains, (b) the variation in composition within the grains, and (c) the concentration of inclusions at the boundaries of the grains.

Whenever an ingot is deformed the shape of the grains is altered. In consequence of this the distribution of the areas of different composition and of the inclusions at the grain boundaries is also altered. As deformation proceeds, the shape of the original grains and the distribution of inclusions and areas of different composition continue to change, and when deformation is completed, the distribution of these is closely related to the way in which the metal has been brought from its initial to its final shape. As soon as the original grains are distorted, however, recrystallization begins and a new generation of crystals is soon produced. Thereafter, there is little connexion between the original grain structure and the new arrangement of smaller crystals that have replaced it. As, however, recrystallization does not affect variations in composition or the distribution of inclusions, it is necessary to consider these as if the effect of working was simply to distort the original grains, and to deal separately with its effects on the crystal structure. Thus the effect of working will first be considered as if the original grains retained their identity, and in this connexion attention will be confined to steel which is the only metal in which the phenomena to be discussed have been extensively studied. The loss of one important feature of the identity of the original grains, i.e. their crystallographic continuity, will be dealt with subsequently in relation to metals in general.

Whether the original grains are columnar or equiaxed, and irrespective

of what happens to their crystal structure, their shape must change in conformity with the change in shape of the ingot. If, therefore, the ingot is extended in length by rolling, the original grains are elongated and the distribution of inclusions becomes such that they may be said to lie on the surfaces of narrow lenticular fibres. This has a pronounced effect on the properties of the metal in different directions. If a given number of inclusions of a particular range of sizes is distributed completely at random throughout a metal, the effect on its properties is a minimum, and is the same in all directions. If, however, they are systematically arranged their effect will tend to increase, and to vary according to the direction in which the measurement is made. If two test-pieces are cut from a rolled bar so that the long axis of one is at right angles, while that of the other is parallel to the direction of working, the difference in the arrangement of the inclusions in relation to the axes of the test-pieces gives rise to marked differences in their mechanical properties. Suppose that they are prepared for an Izod impact test. In the one that has been cut with its axis parallel to the direction of rolling the plane along which fracture will proceed is perpendicular to the sheets and rows of inclusions. Consequently, the distribution of the inclusions does not facilitate fracture. In the other test-piece, however, the sheets of inclusions are parallel to the plane along which fracture will proceed. As the cohesion of the metal is weakened by their presence fracture will readily take place along the line of these sheets. Thus a worked metal is less resistant to fracture along a plane parallel to the direction of working than along one perpendicular to this direction. As the line of fracture of impact, bending, torsion, and tensile test-pieces is perpendicular to the long axis of these pieces, longitudinal give better results than transverse test-pieces.

By consolidating the metal, increasing the cohesion between its parts, and refining its crystal structure, working greatly improves the mechanical properties. Owing to the characteristic arrangement of the inclusions that is produced, however, this improvement is mainly in one direction. If the ingot is just worked sufficiently to promote consolidation, the directional effects of deformation are not appreciable, and its properties are improved in all directions. If, however, working is continued in order to obtain a marked improvement in properties, then this is mainly in one direction. Table 51 (276) shows the effect of different amounts of working on the mechanical properties of a nickel steel. The amount of working performed is expressed as the ratio of the cross-section of the ingot to that of the billet at the stage the test-pieces were taken. The difference between the results from longitudinal and transverse specimens is shown particularly by the Izod tests. This difference increases with the amount of working, but as it is impossible to cut transverse test-pieces when the cross-section becomes small the effects of very heavy reductions cannot be satisfactorily measured. Another illustration of the difference between the longitudinal and

transverse properties of worked metal is given in Table 52 (277), in which the directional effect is shown for the metal as forged and also

TABLE 51

<i>Ratio</i>	<i>Cross-section of ingot</i> <i>Cross-section of billet</i>	<i>Ultimate</i> <i>Tensile</i> <i>Strength</i>	<i>Elongation</i> <i>on 2 in.</i>	<i>Reduction</i>	<i>Izod</i> <i>impact</i>
LONGITUDINAL TESTS					
	1·7	57·9	20	52·5	49
	3·2	58·2	20	58·0	59
	6·1	57·5	22	63·0	72
TRANSVERSE TESTS					
	1·7	57·8	18	64	40
	3·2	57·5	16	61	29
	6·1	57·5	12	55·5	25

TABLE 52

<i>Orientation of</i> <i>axis of test-</i> <i>piece to fibre</i> <i>of steel</i>	<i>Treatment</i>	<i>Ultimate</i> <i>tensile</i> <i>strength</i> <i>tons per</i> <i>sq. in.</i>	<i>Elongation</i> <i>%</i>	<i>Reduction</i> <i>in area</i> <i>%</i>	<i>Izod</i> <i>impact</i> <i>ft.-lb.</i>
Parallel	{ As forged }	97·2	11·7	36·9	10
Transverse		84·5	4·2	12·5	5
Parallel	{ Quenched from 830° C.	62·5	19·0	43·4	34
	{ in oil. Tempered at				
Transverse	{ 600° C., water-cooled. }	59·7	8·0	19·6	9

TABLE 53

Comparison of Transverse and Longitudinal Properties of 6 in. diam. Bar of Steel containing 0·32 per cent. C, 3·44 per cent. Ni, 0·65 per cent. Cr, and 0·12 per cent. Mo. Oil Hardened from 850° C. Tempered at 600° C. and air-cooled.

<i>Property</i>	<i>Mean</i> <i>transverse.</i> <i>Column 1</i>	<i>Longitudinal</i>	
		<i>Central.</i> <i>Column 2</i>	<i>Mean.</i> <i>Column 3</i>
0·1 per cent. proof stress, tons/sq. in.	44·5	44·4	47
Ultimate stress, tons/sq. in.	57·9	57·4	58·6
Elongation, per cent. on 2 in.	13·5	21·5	22·9
Reduction in area, per cent.	36·5	61·0	62·0
Izod impact, ft.-lb.	21·6	40·2	43·0
Hardness, V.P.N.	280	282	284

after quenching and tempering. The effect of direction is most pronounced in the values for elongation, reduction in area, and resistance to impact.

A final example of the directional effect of forging is given in Table 53 (278). This relates to a steel that is used for the manufacture of

forgings of the very highest class such as are employed in aero engines, and shows the difference in the longitudinal and transverse properties in a 6 in. diameter bar. The first column gives the mean values for three transverse specimens. As the mid-length (approximate point of fracture) of transverse specimens passes through the middle of the bar, the second column shows the results obtained with longitudinal test-pieces lying along the centre of the bar. The third column shows the mean results obtained with five longitudinal test-pieces extending across the diameter of the bar. From this table it will be seen that there is not much difference in the values of proof stress, ultimate stress, and hardness obtained on longitudinal and transverse specimens respectively. There is, however, a pronounced difference in the values of elongation, reduction in area, and resistance to impact.

In the case of inclusions that are not plastic at the forging temperature it is only the distribution that is changed by working, and this is what happens to the oxide and silicate inclusions in steel. Plastic inclusions like the manganese-iron-sulphide inclusions in steel are themselves elongated in the direction of working, but whether distribution alone or distribution and shape are changed, the arrangement of inclusions produced by working gives to metal, and particularly to steel, a definite directional structure which is described as 'fibre'. As the properties parallel to the fibre are so much superior to those at right angles to it, the shaping of steel should be carried out in such a way that the fibre will be disposed so as to give the maximum resistance to the stresses applied in service. In other words, the direction of working should be such that tensile stress applied in service will be parallel to the fibre, while bending, torsion, and shearing stresses are perpendicular to it. A simple example is provided by considering the forging of a gear blank in two alternative ways. If a flat bar is rolled down from a billet and the blanks stamped out of this, the fibre produced by the rolling will run straight across the blank. When the teeth are cut the fibre will be longitudinal in some, transverse in others, and in intermediate directions in the remainder. As the principal stress imposed on gear teeth is a transverse shear, those in which the fibre is transverse will be liable to break off. In order to obtain the strongest gear the fibre should be longitudinal in every tooth, i.e. in the blank it should radiate from the centre to the periphery. This condition may be produced as follows: A round bar of a diameter considerably less than that of the blank is made by rolling. A suitable length is then cut off and 'upset', i.e. flattened out in a direction perpendicular to that in which it was previously rolled. During this process the short length of bar is reduced in height and increased in diameter. Expansion is therefore radial and in the finished disc the fibre is radial. When the teeth are cut the fibre is longitudinal in every one of them and there is no transverse weakness.

Arranging the method of working so that the resulting fibre will be

parallel to the direction of tensile stressing and perpendicular to the direction of shear or bending is known as the control of 'grain-flow'. In rolled products the fibre is always parallel to the rolling direction, and in such products, e.g. rails, beams, columns, rods, and wire, this is the correct direction. In forged products, however, the direction of the fibre depends on the way in which the metal is brought from its initial to its final shape, and when there are alternative ways of doing this, as in the case of the gear just described, grain-flow should be taken into account in addition to the easiest method of shaping. In guns and

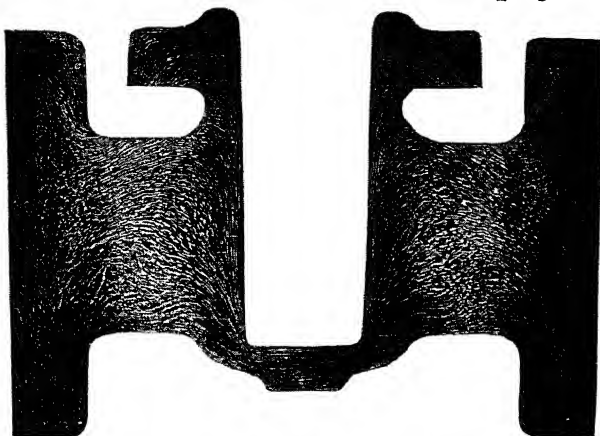


FIG. 259. Macro print of section through a valve body showing grain flow.

(The English Steel Corporation, Ltd.)

pressure vessels, for example, it would be undesirable to have a very pronounced longitudinal fibre, and consequently these should be forged so that there is not too much longitudinal extension (Operation *D*, Fig. 249) or too little circumferential opening-out (Operation *C*, Fig. 249). On a section through a forging the direction of grain-flow can be revealed by deep etching, as shown in the section of a valve body in Fig. 259. This indication of grain-flow by means of etching does not necessarily depend on the distribution of the inclusions, but is probably mainly due to the distribution of areas of different composition. This factor also contributes to the difference between transverse and longitudinal properties and may now be described.

In the grains of the original ingot there is a marked difference in composition between the skeleton and the matrix. When the ingot is deformed, recrystallization begins, and successive generations of new crystals are formed as deformation proceeds. This, however, does not affect the distribution of the areas of different composition which constitute the original skeletons and matrices. The only result of recrystallization is that the space originally occupied by one crystal becomes occupied by many. This is most clearly illustrated when

recrystallization is caused to take place without pronounced deformation. It is then possible by suitable methods of etching to bring up either the original skeleton grain structure, which is determined by variations in composition, or the recrystallized structure, which is determined by variations in orientation. Sometimes both structures may be revealed at the same time, and it is then seen that the area covered by one skeleton and matrix is occupied by numerous crystals. During severe working the skeleton structure is, however, severely distorted and each original grain is drawn out to a thin elongated shape. The original skeletons and matrices are thus transformed into irregular bands of varying composition parallel to the direction of working. As the metal is maintained at an elevated temperature during working there is an opportunity for diffusion to occur, but the extent to which this takes place depends on the temperature and time of heating, the rate of diffusion of the dissolved elements, and the distances over which they must diffuse (i.e. the original grain size). Under suitable conditions rapidly diffusing elements may become substantially uniformly distributed within the space occupied by each original grain. Carbon in steel behaves in this way. Slowly diffusing elements do not do this, however, and the heterogeneity resulting from solidification persists during working. Phosphorus, the rate of diffusion of which is about one-hundredth of that of carbon, behaves in this way in steel.

Owing to the fact that cast steel consists of large grains in which very slowly diffusing elements like sulphur and phosphorus are heterogeneously distributed, the hot-worked metal has bands of different composition running parallel to the working direction. These bands are the result of the distortion of the original skeletons and matrices and constitute the banded structure. Worked steel has therefore three structures: (1) the fibre structure due to the distribution of inclusions and which can be revealed by sulphur prints, (2) the banded structure due to the distribution of areas of different compositions and which can be revealed by deep etching, and (3) the microstructure which consists of austenite grains above the critical range and ferrite plus pearlite below it. It is because of structures (1) and (2) that worked steel has such strongly marked directional properties and these two structures together constitute its macrostructure. Steel cooled without working has also a macrostructure and microstructure, but in this case the macrostructure shows the skeleton and matrix of each original grain and the arrangement of these grains in the casting, while the microstructure consists of the ferrite and pearlite formed during cooling. The macrostructure of the cast metal also shows segregation in the casting as a whole and this is also a feature of the macrostructure of the worked metal.

Of the three aspects of the original structure mentioned at the beginning of this section it remains to discuss the effect of working on the crystallographic continuity of the original grains. It has already

been stated that under the conditions realized in hot-working the deformation of these is soon followed by recrystallization. The new generation of crystals thus produced is in turn deformed and another new generation appears. Thus, as long as working continues deformation and recrystallization are going on. As the deformation of metals tends to promote recrystallization, and time favours crystal growth, the size of the crystals decreases with increase in the amount of deformation performed in a given time. After the working operation is completed, however, no more generations of new crystals appear. Consequently, crystal growth takes place unhindered as the metal cools. The rate of this growth increases with the temperature, while the amount of growth increases with the time taken to cool to the lowest temperature at which growth proceeds at an appreciable rate. In order to obtain the smallest crystals it is therefore necessary to continue the working operations down to as low a temperature as other conditions permit and then to cool as rapidly as is convenient. Owing to the fact that the metal becomes stiffer as it cools, and is more liable to exhibit the effect of hardening by working, rolling and forging cannot always be continued to as low a temperature as a consideration of the optimum crystal size would indicate as desirable. Small articles may, however, be worked at lower temperatures than large ones, and as they possess the further advantage of cooling more rapidly they usually display a much finer structure. In metals which undergo a constitutional change affecting the whole mass at a temperature below that at which the working operations are completed, the temperature at which working is stopped does not directly control the crystal size. During the working of steel, e.g., the operation is usually discontinued before the metal enters the critical range. This is not universally true, for stock of small size is frequently worked as it passes through the critical range, but when rolling or forging is stopped above this range it can only affect the size of the austenite crystals. Under these conditions the change from austenite to ferrite and pearlite is not directly affected by the working operations. As, however, the fineness of the ferrite-pearlite structure depends on the size of the austenite grains and the rate of cooling, the temperature at which working is finished has the same effect as in metals that undergo no constitutional change below the working temperature.

Several factors in addition to those described have to be taken into account when the metal concerned consists of two constituents. If the metal is to be worked one of the constituents must be malleable in the hot-working range. If the other is also malleable the effects of working are not very different from those just discussed, and attention may therefore be confined to the conditions that arise when the second constituent is brittle at the working temperature. The behaviour of such an alloy depends on the properties of the two constituents, their relative amounts, and the way in which they are distributed; and in this connexion much depends on the relative continuities of the two

constituents. Various examples of the behaviour during working of alloys of this kind are considered in Chapter VI. For the present purpose the types of structures that need to be discussed are:

1. Alloys that consist of ductile primary crystals of a pure metal or solid solution and a brittle constituent in the free state which may be in the form of (a) more or less continuous films, or (b) isolated globules at the boundaries of the primary crystals.
2. Alloys that consist of ductile primary crystals as above and a eutectic which wholly or partly isolates them and in which the brittle constituent is (a) continuous or (b) discontinuous.

An example of 1 (a) is provided by copper containing a small amount of bismuth, of 1 (b) by copper containing oxygen, of 2 (a) by iron-carbon alloys containing more than 1.7 per cent. of carbon, high-speed steel, and aluminium-copper alloys containing more than 6 per cent. of copper. Finally, an example of 2 (b) is provided by aluminium-silicon alloys. All these are considered in Chapter VI.

In alloys of types 1 (b) and 2 (b) the brittle constituent occurs either in the free state or in a eutectic as discontinuous particles. In this form it interferes with working to some extent and its effect increases with the amount. The interference is not serious, however, because deformation occurs in the continuous plastic constituent which flows round the other. In alloys of type 1 (a), however, the brittle constituent tends to be continuous and the continuity increases with the amount, while in alloys of type 2 (a) the brittle constituent is always continuous in the eutectic but the continuity of this increases with the amount. As the continuity of the brittle constituent increases, working rapidly becomes more difficult, beyond a certain point it becomes impossible unless very carefully performed, and with a further increase in the amount of the brittle constituent it may become impossible under any conditions. This is because the brittle constituent breaks up during working. If it is sufficiently continuous the metal as a whole fractures, if it is less continuous its break-up results in the ductile constituent becoming more continuous. Thus, if an alloy of this kind can be worked at all, the working breaks up the brittle constituent and establishes the continuity of the other. Subsequent working is then comparatively easy. It is because of this factor that high-speed steel, iron-carbon alloys containing up to 2.6 per cent. of carbon, and aluminium-copper alloys containing up to 8 per cent. of copper can be worked if sufficient care is taken.

It remains to discuss the effect of working when it is carried out in a range in which a constitutional change is taking place in a metal. In steel containing more than 0.9 per cent. of carbon, cementite separates from solution during cooling. If the metal is cooled without working, this forms envelopes round the austenite crystals and plates along their crystallographic planes. The final cementite-pearlite structure is therefore brittle. If, however, the metal is worked while the cementite is forming, a very different structure is obtained. Under these conditions

deformation and recrystallization are continually taking place in the austenite grains, and the positions of crystal boundaries and planes are constantly changing. Consequently, there is no well-defined system of boundaries and planes at which cementite can form. Furthermore, the cementite that separates from solution is broken up as it forms and the final result is that it occurs as dispersed particles which become globules under the action of surface tension. The resulting structure consists of isolated cementite globules in a pearlite matrix and this has very different properties from that formed when no working is performed. Forging while cementite is forming is an important feature of the treatment of carbon tool steels. The conditions are different when the steel contains less than 0.9 per cent. of carbon because the ferrite then formed is not brittle and is not broken up. Nevertheless, even in these steels working in the critical range affects the structure. In the case of steels containing less than 0.35 per cent. of carbon, which normally consist of isolated areas of pearlite in a matrix of ferrite, the principal effect of such working is a decrease in the size of the ferrite crystals. Steels containing more than 0.55 per cent. of carbon consist normally of ferrite envelopes outlining the austenite grains and enclosing areas of pearlite. The distribution of the ferrite is affected by working while it is forming, because owing to deformation and recrystallization of the austenite there is no fixed system of crystal boundaries at which ferrite can form. Consequently, the ferrite appears as small isolated crystals instead of as boundary envelopes. Working down to the lower limit of the critical range is possible only when the stock is small, and working below it is rarely carried out in hot-working operations. If, however, this is done, then the cementite lamellae in pearlite will be broken up and tend to globularize.

Heat Treatment After Hot-working.

Throughout the discussion of hot-working it has been assumed that recrystallization keeps pace with deformation to such an extent that no strain-hardening results. Actually, however, the capacity of metals for strain-hardening cannot be regarded as zero except at temperatures near the melting-point. When, therefore, a metal is hot-worked it may be strain-hardened to an extent that increases as the working temperature decreases, as the amount of deformation performed in a given time increases, and as the time taken to cool from the working temperature decreases. If heavy working is continued down to the lower limit of the hot-working range the metal after working may be considerably strain-hardened. Annealing after working may therefore have the effect of eliminating this and softening the metal. Apart from this annealing may be carried out to eliminate internal stress, and steel may be normalized to eliminate stress and refine the structure. Finally, steel and aluminium alloys may be subjected to the usual treatments such as hardening and tempering and solution-treatment and ageing.

THE REMOVAL OF SCALE

During the hot-working operations and the heat treatments that necessarily accompany them, coatings of scale are formed on all the common metals except aluminium and its alloys. By controlling the atmosphere in which the metal is heated the loss of appreciable quantities may be avoided, and the scale formed during these operations is in any case largely detached during working. But the atmosphere in which the working is performed cannot as yet be controlled, and although efforts are made to remove scale during working by spraying with water and by other means, there is always a coating of oxide on the products of the forge or rolling-mill. A considerable amount of steel goes into service straight from the hot-working operations and is painted without de-scaling. Whenever a good surface is required, however, the scale must be removed. It is therefore frequently necessary to de-scale hot-worked metal before it goes into service, and it may then be used in this condition or after painting. When the hot-working operations have to be followed by cold-working, machining, polishing, or when the metal has to be tinned, galvanized, enamelled, or electro-plated, scale removal is again essential. At various stages in cold-working the metal may be annealed, and unless this is carried out in an atmosphere which prevents oxidation, another layer of scale is formed. Consequently, inter-pass annealing is frequently followed by de-scaling. Finally, scale may also be formed during final heat treatments such as normalizing and hardening, and it is therefore safe to say that most metallic articles are de-scaled once, and frequently more than once, before they reach the ultimate consumer.

Three methods are available for the removal of scale: (1) by reduction of the oxide by heating in hydrogen, (2) by abrasion, and (3) by pickling. Heating in a strongly reducing atmosphere is employed to some extent in order to avoid the formation of scale during inter-pass annealing and the final heat treatment, but it is not yet used to any appreciable extent for removing scale that has been produced during hot-working. Abrasion is more extensively employed, and at the present time practically all de-scaling may be said to be accomplished either by abrasion or by pickling, and mainly by pickling. The methods available for the removal of scale by abrasion consist of tumbling, scratch-brushing, and blasting. The first method consists in agitating the articles to be cleaned in a vessel containing sand. It is widely used for removing scale from castings, but this consists in the main of fritted sand, which is comparatively easy to remove. The method is not very effective, however, in removing oxide scale except from articles of simple shape. Scratch-brushing is expensive and is mainly applicable to cleaning light articles that have been slightly scaled. Abrasive blasting is, however, a method that is capable of wide application, and for many purposes it competes successfully with pickling. Sand is the

usual abrasive, but steel shot and other abrasives can be employed. By this method scale can be satisfactorily removed from articles of simple contour, but it is not usually successful in completely removing the scale from intricate parts. One objection to the process is that it tends to polish rather than remove thin adherent scales, and thereby to conceal rather than reveal surface defects. Another drawback is the cost. Plant for abrasive blasting is expensive to instal, and the cost of operation and maintenance is high. Nevertheless, it is displacing pickling in some directions. This does not in itself imply any general superiority from the point of view of economy or efficiency of abrasive blasting compared with pickling. There are too many factors involved in the cleaning of metals and too little is known about their relative importance to make any general comparison of the available methods possible. It simply means that at the present time certain plants, after considering their own conditions, their pickling practice, and the extent to which, in the light of their own knowledge, they think this practice could be improved, have substituted abrasive blasting.

Pickling in acid is the method most widely employed in de-scaling metals, and until quite recently little was known about the mechanism of this process. If the scale were soluble and the metal insoluble in the pickling acid, e.g. hydrochloric or sulphuric, the process of de-scaling would require little explanation. But the metal is generally more soluble than the scale, which sometimes does not seem to dissolve to an appreciable extent and is simply detached. When scaled metal is immersed in acid this has access to the metal surface through cracks and pores in the scale, and the first acceptable view of the mechanism of scale removal supposed that it was forced off by the pressure of the hydrogen generated at the metal surface. This explanation accounted for scale removal but made it difficult to account for the action of 'inhibitors' or 'restrainers' which are substances added to the pickling bath to prevent acid attack on the metal. A more recent explanation suggested by Winterbottom and Reed (279) is now, however, generally accepted as far as steel is concerned. As explained in Chapter VIII the scale formed on steel above 570°C . consists of three layers, an inner one consisting mainly of FeO , an intermediate one consisting mainly of Fe_3O_4 , and an outer one consisting mainly of Fe_2O_3 . By subjecting scale to the attack of pickling acid it was shown that the inner layer of ferrous oxide is soluble. Consequently, it is now considered that the removal of scale depends on solution of the inner layer by the acid followed by the flaking off of the outer layers.

Scales formed at temperatures below 575°C . contain no ferrous oxide and their removal cannot be explained in this way. These are thinner and much more difficult to remove than those formed at higher temperatures, and it appears that the mechanism of their removal may be as suggested by Hoar (280). The conditions obtaining at a crack or pore in the scale are illustrated diagrammatically in Fig. 260. Under the

conditions realized, a cell, scale|acid|metal, is set up in which the oxide is the cathode and the metal the anode. Iron dissolves at the anode, forming a ferrous salt, while hydrogen ions appear at the cathode and reduce the ferric to ferrous oxide, which then dissolves in the acid, exposing fresh ferric oxide for cathodic reduction. Since this electrolytic action is most pronounced near the scale-metal interface the main solution of scale and metal occurs in the regions shown by the dotted lines in Fig. 260. Thus the scale is undermined and eventually flakes off.

For the pickling of steel, either sulphuric or hydrochloric acid is generally employed, but mixtures of hydrochloric and nitric acids are frequently used for pickling stainless steels, and sometimes a second pickle in nitric acid alone is used to produce a pleasing surface. For

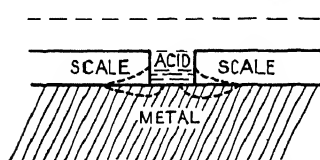


FIG. 260. Conditions realized at pore in scale.

(Hoar.)

cleaning tools that have been lightly scaled during tempering, immersion for long periods, e.g. eight hours, in acetic acid followed by mud blasting is sometimes used because this weak acid does not affect the surface of the steel. Chromic acid is used for cleaning lightly scaled nickel alloys, and for thicker scales baths of nitric or nitric and sulphuric acids are employed. The strength of the original bath varies according to the acid used, the scale to be removed, the metal concerned and the practice of the plant. With hydrochloric acid a common strength is 50–100 gm. of acid per litre, whilst 30–60 gm. per litre is a common strength for sulphuric acid baths. The acid strength diminishes as a result of acid being used in dissolving the metal and the scale. From time to time during working fresh acid is added to replace that used up, but the concentration of metallic salts increases continuously while the bath is in use, and the whole must finally be discarded and a fresh bath made up. Pickling baths are usually operated at an elevated temperature, e.g. from 30° to 40° C. in the case of hydrochloric acid and 60° to 70° C. in that of sulphuric acid. The bath is heated by injecting steam which also promotes agitation.

The complete removal of scale requires that the metal shall be immersed in acid for a certain length of time (usually about 20 to 30 minutes) and during this an appreciable amount of metal may be dissolved. Furthermore, as the attack of the acid is not uniform the surface of the metal is pitted, and the solution of metal uses up acid and hastens the exhaustion of the bath. To prevent these effects certain substances known as 'inhibitors' or 'restrainers' are added to prevent reactions between the metal and the acid. The commonest restrainers are simple colloids such as glue, gelatin, or flour, but most of the commercial products contain as their principle constituent organic compounds of nitrogen. The mechanism of inhibition depends on the adsorption of these substances by the metal surface and this in turn

prevents the acid-metal reactions. An investigation of the effect of restrainers has recently been reported by Swinden and Stevenson (281) in which they conclude that efficient restraining is necessary when pickling with hot sulphuric acid, but in the case of cold hydrochloric acid the rate of attack on the metal is small in the absence of any restrainer. Certain restrainers are, however, capable of reducing this attack practically to zero.

The acid which remains on the surface of the metal and particularly in minute fissures and crevices, tends to initiate corrosion after pickling. To some extent this is avoided by thorough rinsing followed by immersion in a bath of lime-water to neutralize any acid remaining. If the acid is not completely removed or neutralized the metal will corrode more rapidly than otherwise, and in order to eliminate any danger of this, pickling is sometimes performed in phosphoric acid which tends to prevent rather than promote corrosion. Obviously, a small amount of acid adhering to metal cannot be responsible for continuous corrosion, but it can easily destroy a good surface, and as the further progress of corrosion depends to a marked extent on its initial stages, even a small quantity of acid may lead eventually to serious consequences.

One aspect of pickling that has aroused considerable attention is the absorption of hydrogen by steel. This sometimes results in the formation of blisters during pickling and more frequently in embrittlement of the metal. It was shown by Fuller (282) that hydrogen readily penetrated iron at temperatures of from 20° to 100° C. when it was pickled in 1 per cent. sulphuric acid. By an ingenious experiment Edwards (217) subsequently showed that the hydrogen liberated at the surface of contact between steel and acid could diffuse with considerable rapidity through the metal. The hydrogen thus picked up by steel immersed in acid or subjected to electrolytic action is in the atomic (i.e. nascent) state in which it can readily diffuse through the metal. While hydrogen is being liberated at its surface the steel is rendered brittle by the atomic hydrogen that diffuses into it, and this can be demonstrated by testing the steel while immersed in acid or immediately after withdrawal. Once the production of atomic hydrogen at the metal surface is stopped, absorbed hydrogen begins to diffuse out again, and after a few days at atmospheric temperature or about 30 minutes at 100° C. the metal recovers most of its original ductility. The embrittling effect of the hydrogen is thus, in general, a temporary phenomenon. If, however, the hydrogen has an opportunity of coming out of solution in the metal, and accumulating in small cavities or at the surface of contact between metal and inclusions, then combination between hydrogen atoms takes place and the molecular hydrogen thus produced does not diffuse out again. As atomic hydrogen continues to diffuse into such cavities while molecular hydrogen cannot diffuse out, high gas pressures are built up, and these may have the effect of producing surface blisters or permanent brittleness. Thus, in general, steel is rendered brittle

when immersed in pickling acid. This brittleness tends to disappear after withdrawal from the acid and does not have serious consequences unless the steel is subjected to cold-working without previous heating or allowing the metal to rest to permit elimination of the hydrogen. If, however, the steel is in a condition of internal stress when immersed in the acid, the combined effects of this stress and absorbed hydrogen may cause the formation of cracks. Furthermore, if the hydrogen has the opportunity of changing to the molecular form in cavities in the metal then blisters and permanent brittleness may result. Other effects arise from the absorption of hydrogen by steel during heat treatment and melting and these are considered in Chapter XII.

Sutton (283) investigated the effect of the composition and treatment of the steel on the degree of brittleness induced by pickling for 30 minutes in 10 per cent. sulphuric acid maintained at a temperature of 50° C. He found that whatever the composition or treatment of the steel, the brittleness was substantially removed by immersion in boiling water for 30 minutes or allowing the metal to stand at atmospheric temperature for four or five days. In general, the susceptibility of carbon steels to hydrogen embrittlement was found to increase with the hardness. Mild-steel strip (0.11 per cent. carbon) in the annealed condition, i.e. furnace-cooled from above the critical range, was not perceptibly affected by pickling, and the same material in the normalized condition, i.e. air-cooled from above the critical range, was only slightly affected. Cold-working or water-quenching increased the susceptibility to embrittlement. The effect of treatment was found to be the same when a medium-carbon (0.46 per cent.) and a high-carbon (0.85 per cent.) steel were studied. With these steels, reheating after quenching or cold-working was accompanied by a progressive decrease in susceptibility as the reheating temperature was raised. An alloy steel containing 0.18 per cent. of carbon, 3.78 per cent. of nickel, and 1.16 per cent. of chromium was found to be less susceptible to brittleness than either the medium- or the high-carbon steels. Sutton discovered that the most pronounced effect was obtained when the steel was deformed after quenching, or after quenching followed by tempering at a low temperature. After this treatment samples of the medium and high-carbon steels developed cracks at the deformed places, and some even fractured during pickling. This effect was not obtained with the mild steel or the alloy steel, but in this connexion it is interesting to note that Monypenny (284) recommends that stainless steel should not be pickled in the hardened condition because being in a state of internal stress it is liable to develop surface cracks.

The mechanism of hydrogen brittleness has been the subject of much speculation. Frequently, embrittled iron or steel fractures along the crystal boundaries instead of through the crystals in the normal manner of ductile material. On this account it has been suggested that the hydrogen absorbed diffuses mainly along the crystal boundaries and

decreases cohesion at these points. It has been shown, however, by Edwards and Smithells and Ransley, that hydrogen diffuses through a single crystal just as readily as through an aggregate, and it may therefore be inferred that the absorption of the gas is not a phenomenon peculiar to the crystal boundaries. Nevertheless, although hydrogen diffuses with equal facility through crystals and along boundaries, there may be a tendency for dissolved hydrogen to accumulate at boundaries and decrease the cohesion there by building up a pressure. Under the conditions realized in pickling, this stress is not in itself sufficient to produce cracks or rupture, but if the metal is already in a state of internal stress due to cold-working or rapid cooling, the additional stress set up by the hydrogen absorbed is sufficient, in some cases, to lead to cracking or even fracture. The same applies to external stress applied while the metal is in the acid or soon after withdrawal. The steel, which is already in a state of internal stress due to the hydrogen, does not deform to the normal extent and thus behaves like a brittle material.

Another effect of the absorption of hydrogen during pickling is the formation of blisters on thin sheet. These are sometimes encountered during the manufacture of tin-plate, and they make their appearance while the sheet is in the pickle or during subsequent annealing. They are small in size and form in large numbers, giving the surface a pimpled and rather dull appearance. Several investigators have studied this phenomenon, and the most satisfactory explanation is that due to Edwards (217) who supported the claims of his hypothesis by means of careful experiments. According to him, blisters are produced on thin sheets when the diffusion of hydrogen through the metal is interrupted by inclusions. On the one hand hydrogen liberated at the surface of steel immersed in acid is nascent, i.e. atomic, and it is because of this that it can diffuse so readily through the metal at temperatures close to atmospheric. Molecular hydrogen on the other hand cannot diffuse through steel at ordinary temperatures. Edwards's hypothesis is that when the diffusion of the hydrogen from the surface is interrupted by an inclusion, the gas tends to accumulate between the metal and the surface of the inclusion. In this place combination of hydrogen atoms to form molecules takes place. As these cannot diffuse away the gas pressure in the neighbourhood of the inclusion continues to rise as more atomic hydrogen diffuses inwards. Finally, if the thickness of metal between the inclusion and the surface is sufficiently small it is expanded outwards and forms a blister. It is probable that the same effect would be produced by the accumulation of molecular hydrogen in the cavity of an incompletely welded blowhole or other defect, and the fact that high pressures can be produced in this way has been demonstrated by Bardenheuer (287). A mild steel bar was bored out longitudinally to form a thick-walled cylinder closed at one end, and a pressure-gauge was fixed tightly into the open end. Hydrogen was generated at the outer surface of the steel by electrolysis, and after a short time, the gas

pressure in the inside rose to 4,300 lb. per sq. in. when the experiment had to be discontinued because the limit of the pressure-gauge had been reached.

COLD-WORKING

Except in so far as the metal may become heated by the deformation, cold-working is carried out at atmospheric temperature. At this temperature the effects of deformation are substantially permanent in the metals iron, copper, aluminium, nickel, magnesium, and their alloys, and it is on this fact that the characteristic effects of cold-working depend. In the case of the metals lead, tin, and zinc and some of their alloys, recrystallization can proceed fairly rapidly at atmospheric temperature, and these metals are not affected in the same way as those just mentioned. Thus, in considering cold-working, lead, tin, and zinc can be excluded, for the working of these at atmospheric temperature actually resembles the hot-working of the other metals.

When iron, copper, aluminium, nickel, magnesium, and their alloys are deformed at atmospheric temperature the changes considered in Chapter III are produced. Under the action of the applied force the metal changes its shape and the shapes of the constituent crystals alter in conformity with it. If the extension of the metal is in one direction only, as in rolling-rod or drawing-wire, the crystals are elongated in the direction of working, and if this is sufficiently severe the original equiaxed crystals assume long fibre-like shapes as shown in Figs. 52 and 54 (pp. 128, 129). This structure is sometimes referred to as the fibre and must be distinguished from the fibre structure produced in steel by hot-working. The change in shape of the individual crystals takes place by slip on the crystallographic planes as described in Chapter III, and this is accompanied by several changes in the crystal structure and orientation which are also described in Chapter III. For the present purpose the only effects of deformation that need be considered are (a) the strain-hardening and (b) the instability which leads to recrystallization when the deformed metal is heated.

By means of cold-working it is possible to roll thinner sheets and strip, to draw tubes of smaller diameter and thinner wall thickness than can be produced hot, and to draw wire. Further, it is possible to work to more accurate sizes and to produce a better surface finish. In considering the application of this process these factors have to be taken into account in addition to the change in mechanical properties that may be produced in this way. In some cases the object of cold-working is simply to produce articles of accurate size or good surface finish, as in the manufacture of bright drawn-bar or cold-rolled strip. In other cases the primary object is to produce the requisite change in shape, as in the stamping and pressing of parts out of sheet, and in still other cases the alteration of mechanical properties is almost as important as the change in shape, e.g. in the manufacture of high-strength wire and certain pressed articles.

The cold-working operations are generally associated with several heat treatments which are performed before, during, and after the working. Generally, these treatments are simple annealings involving heating above the recrystallization temperature. When performed before working the object is to eliminate internal stress resulting from casting or hot-working and to soften the metal in preparation for cold-working. At intermediate stages in the working, annealing is again employed to eliminate the hardening caused by the work in order that further deformation may be possible, and after the change in shape is complete, the metal may again be annealed to restore it partially or completely to the soft condition before going into service. In certain cases, however, treatments other than simple annealing are employed in connexion with cold-working. The high-carbon steel containing about 0.75 per cent. of carbon that is used in the manufacture of high-strength wire is not suitable for drawing when in the annealed condition. It is therefore subjected to a special treatment known as 'patenting'. After the cold-working operations steel wire or strip may be heated to a temperature between 100° and 350° C. in order further to increase its strength and elasticity. This is known as 'blueing'. In addition to this any steel product shaped by cold-working may be normalized or hardened and tempered, and the age-hardening alloys of aluminium may be subjected to this treatment either before or after cold-working.

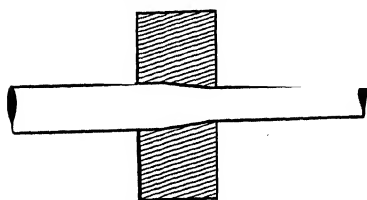
Methods of Cold-working.

The methods employed in the cold-working of metals consist of rolling, drawing, pressing, stamping, and spinning. Cold-rolling is carried out in essentially the same way as hot-rolling, plain cylindrical rolls being used for sheets and grooved rolls for sections. As the common metals are much stiffer at ordinary temperature than at the elevated temperatures at which hot-working is performed, the amount of reduction that is performed in each pass is considerably less, and except when the metal is fairly thin the effect of the working is largely superficial. With many of the non-ferrous metals substantial changes in shape are brought about by cold-rolling, and in fact the mechanical treatment of α -brass is largely confined to working at ordinary temperature; but with steel, cold-rolling is generally employed with the object of producing accurate dimensions and good surfaces.

In the operation of cold-drawing the metal is reduced in cross-section by drawing through a tapered hole. This method may be used instead of cold-rolling in order to finish sections of any shape. Thus it is used for producing 'bright bar' and for finally shaping a variety of sections such as those intended for turbine blades. The most characteristic cold-drawing operation is, however, the manufacture of wire. This can only be performed in the cold. It is true that tungsten wire is drawn at temperatures above 600° C., but it must be remembered that the term cold-working means in general working at temperatures at which

rapid recrystallization does not take place. At temperatures above 600°C . tungsten behaves in accordance with this definition and it may therefore be drawn into wire. With the common metals, however, drawing operations can be performed to a limited extent only at elevated temperatures. In order that the reduced section emerging from the die may be able to transmit the pull required to draw the remainder through, strain-hardening must be produced. A limited amount of drawing may be performed on steel tubes heated to about 850°C ., but when large reductions are required the metal must be cold.

Wire made from such metals as mild steel, high-carbon steel, stainless steel, copper, brass, bronze, aluminium, tungsten, nickel-copper, and nickel-chromium has a wide variety of uses. Most of this is of circular



c. 261. Sketch of wire and drawing die.

cross-section, but flat wire is used for electrical resistances and winding guns, while wire of special shapes is employed in the manufacture of locked-coil ropes. The details of the process vary with the metal being drawn and the purpose for which it is intended; but whatever the variations in the programme of drawing and

annealing, the general features of the wire-drawing operation are essentially the same. The raw material of the wire mill is hot-rolled rod about 0.25 to 0.5 in. in diameter supplied in coils. After suitable heat treatment and de-scaling, this rod is reduced in section by drawing through a series of tapered holes until the requisite diameter is obtained, or until it is hardened to such an extent that another heat treatment is necessary. In single-hole drawing each pass is a separate operation. The rod is first pointed, pushed through the hole, then drawn through by a shackle and attached to a drum. This is then rotated, the wire is drawn through and winds on to the drum. Later, the same procedure is repeated using a smaller hole, and so on until the requisite size is obtained. In continuous drawing the wire is threaded through the first hole, and given a certain number of turns round a drum, then through a second hole and round a second drum, and so on to a maximum of about nine holes. Continuous drawing is more economical than single-hole drawing and is used extensively in the manufacture of non-ferrous wire and also of steel wire to be used under conditions where the mechanical properties are not of paramount importance. For wire ropes, however, wire produced by single-hole drawing is preferred.

The draw-plates or dies used in the manufacture of steel and non-ferrous wire are made of white cast iron, high-carbon or alloy steels, or tungsten carbide, but very fine non-ferrous wires are frequently drawn through diamond dies. Generally, the hole through which the wire is pulled (Fig. 261) consists of a tapered portion in which the reduction in section is produced, and a parallel portion which gives the correct size

to the emerging wire and supports the narrow end of the taper, which otherwise would readily be destroyed by the forces exerted on it. The reduction in cross-section is brought about by the circumferential pressure of the die induced by the direct-tensile pull employed to draw the wire through. The effective part of the die is the portion between the narrow end and the point at which the diameter of the hole equals that of the incoming wire. This is known as the bearing, and the angle of taper and the length of the bearing determine the amount of reduction accomplished in the pass. A given reduction in one pass may be obtained with a short bearing and a steep taper or a long bearing and small taper, but in general a taper of about 6° gives the best results. A given total reduction may be obtained either by a small number of heavy passes or a large number of light passes.

The operations involved in drawing a rod down to wire of the size required constitute the programme of reduction, and the art of wire-drawing depends on the choice of suitable tapers, bearings, reductions per pass, speed of drawing, and total reduction between heat treatments, in accordance with the properties of the metal being drawn and those required in the product. The lubrication of the wire is also of great importance. When a bright surface is not required, steel rod for wire-drawing, after pickling, washing, and dipping in lime, is allowed to rust under a water-spray so that its surface becomes coated with a mixture of lime and ferric oxide. Just before entering the die the wire passes through a box containing pieces of hard soap. This is the lubricant, but the lime and ferric oxide on the surface of the wire cause it to pick up and retain a thin coating of the soap. When a bright surface is required the wire is given a thin coating of copper by immersing in a solution of copper sulphate and is lubricated with oil.

Cold-drawn tubes are produced from hot-finished seamless tubes in somewhat the same way as wire is manufactured from hot-rolled rod, and this operation is employed when it is required to obtain tubes of smaller diameter or wall thickness, of more accurate size, better finish, or higher strength than those which result from hot-rolling. The extensive purposes for which tubes are employed may be divided into two groups. In the first of these may be included those applications in which tubes are used for conveying gases or liquids, or protecting or covering something else. The second contains those in which they are used on account of their advantages as structural components. The first group comprises pipes used for the transportation of gas, oil, and steam, condenser tubes, boiler tubes, electrical conduits, and all those employed in handling gases and liquors in chemical industry; the second comprises those uses in which tubes are employed because the annular cross-section gives greater stiffness and rigidity in comparison with solid sections of equivalent weight. Tubing used for this latter reason is sometimes referred to as 'mechanical' tubing. It is widely used in the cycle, motor, and aircraft industries and is generally cold-drawn.

In cold-drawing tubes the hot-finished product is pointed and the point passed through a tapered hole and gripped by a suitable shackle attached to an endless chain. In this way the tube is drawn through the hole. If the operation is intended simply to obtain an accurate size, a true circular section, or a good finish, one pass is sufficient. But if the object is to produce high-strength, thin-walled, or small-diameter tubes a series of passes is required. Sometimes the operation is performed without a mandril, and when one is employed it is inserted through the incoming tube so that its end just reaches the outgoing edge

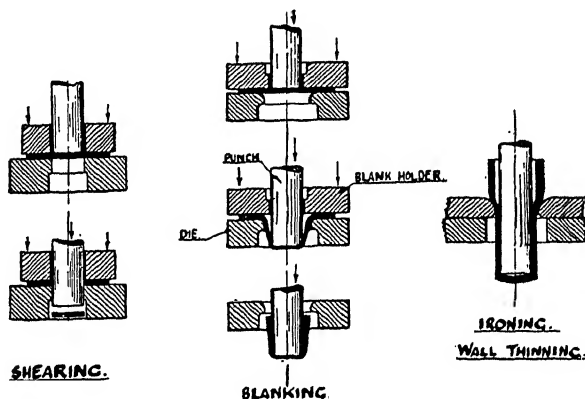


FIG. 262. Diagrams illustrating typical press operations.
(Reproduced by the courtesy of Prof. R. S. Hutton and the
Worshipful Company of Goldsmiths.)

of the hole (Fig. 257). By controlling the amount of reduction after the last heat treatment, or the temperature at which the tube is annealed after drawing is completed, the strength and ductility of the product is adjusted. When steel tubes are finally normalized, the rate of cooling increases with decrease in the wall thickness, and consequently thin-walled tubes have a greater strength per unit of metallic cross-section than thick-walled tubes. When tubes are subject to corrosion, as is frequently the case, their life depends to a large extent on the wall thickness. Under those conditions decreasing the wall thickness in order to obtain greater mechanical strength is liable to prove a serious disadvantage.

At the present time the production of articles by shearing, cupping, and drawing in hydraulic or mechanically driven presses constitutes a very extensive industry, and a large proportion of the product is absorbed in motor-car manufacture for bodies, fenders, wheels, brake drums, bearing cups, &c. Pressings may be made in copper, brass, aluminium, nickel, cupro-nickel, zinc, and mild steel, and they are used for metal furniture, milk-cans, domestic utensils, gas and electric cookers, lighting fixtures, petrol pumps, washing machines, cartridge

cases, bullet envelopes, cylinders, and a large variety of decorative metallic articles.

The typical press operations are illustrated diagrammatically in Fig. 262. The diagrams on the left show the operation of shearing or blank-

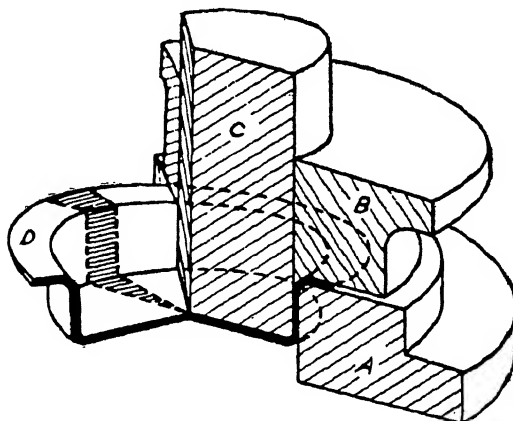


FIG. 263. Cupping. (A) Part of drawing die, (B) blank holder, (C) punch, (D) cup.
(Copper Development Association.)

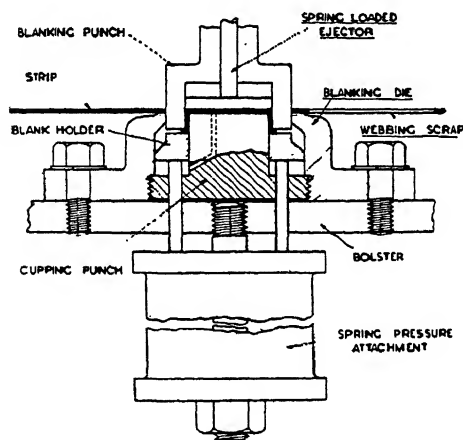


FIG. 264. Combination tools for blanking and cupping.
(Copper Development Association.)

ing by means of which a disc of the requisite size is punched from sheet or strip. Those in the middle illustrate the cupping operation and that on the right shows the drawing process. The relations between the die, punch, and blank holder in the cupping operation are shown in greater detail in Fig. 263, and Fig. 264 shows a combination tool for blanking and cupping. The functions of the die and punch are obvious and that

of the blank holder is to exert pressure on the edges of the blank to prevent wrinkling. The importance of this is illustrated by Fig. 265 which shows the effect of increasing blank-holder pressure in eliminating



g. 265. Influence of blank holder pressure on wrinkle formation.
(Copper Development Association.)

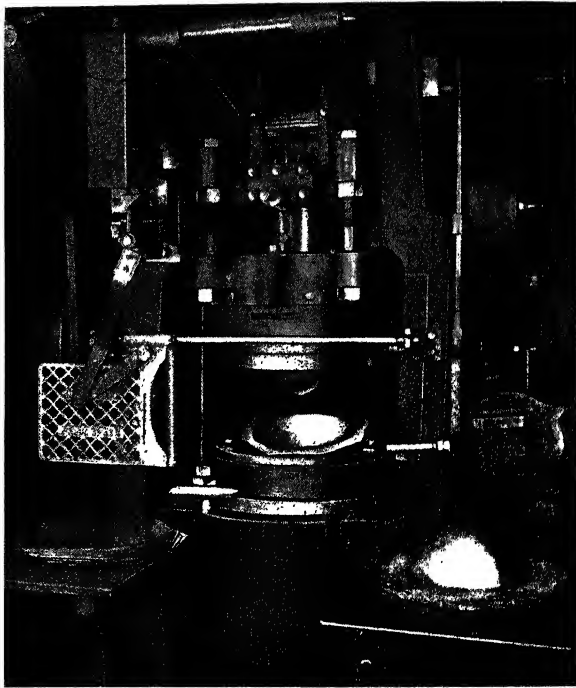


Fig. 266. Press forming headlamp reflectors from octagonal blanks.

(Copper Development Association.)

wrinkling. Fig. 266 shows a press forming headlamp reflectors from octagonal blanks.

Usually the production of the finished article requires a series of press operations each of which changes the shape to a certain extent, and Fig. 267 shows the various stages involved in the production of a fire-extinguisher body. At certain stages intermediate annealing operations are required to eliminate the hardness induced by the working, and circular articles are frequently spun in order to remove wrinkles and

produce a smooth shape. Spinning may also be used to produce constricted parts on plain cylinders formed in the press. In this way the necks are formed on gas cylinders, pitchers, and vases. Other uses are in the production of complicated shapes as shown in Fig. 268.



FIG. 267. Stages in the pressing of a fire-extinguisher body.

(Copper Development Association.)

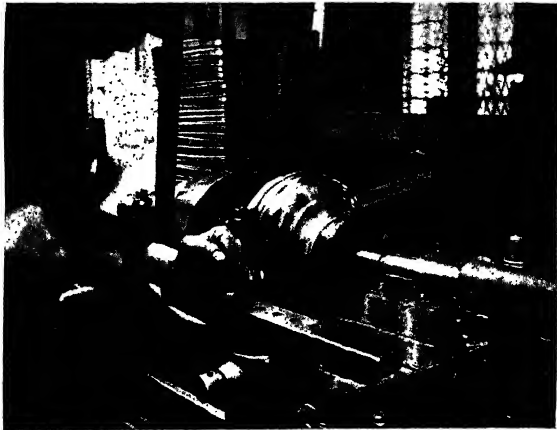


FIG. 268. A typical spinning operation.

(Copper Development Association.)

The Effects of Cold-working and Annealing.

The effects on the crystal structure and mechanical properties of cold-working and subsequent heating have been described in detail in Chapters III and IV. For the present purpose attention may be confined to the most important aspects of these effects. In the first place, the metals that do not recrystallize at atmospheric temperature are

hardened by working, i.e. the tensile strength and yield-stress are raised, the elongation and reduction in area are lowered and the stress-strain curve is made steeper. The amount of deformation to which a metal is subjected is most conveniently measured by determining the extent to which the cross-section is reduced by the cold-working operations. In the case of round material the amount of deformation is expressed as the percentage reduction in cross-sectional area, in the case of strip or sheet it is expressed as the percentage reduction in thickness. If the amount of deformation thus expressed is plotted against the hardness, tensile strength, yield-stress, elongation, &c., an idea of the relations

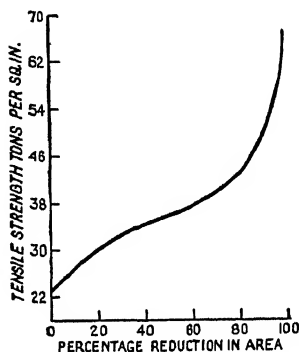


FIG. 269. Effect of wire-drawing on mild steel 0.11 per cent. C. (Pfeil.)

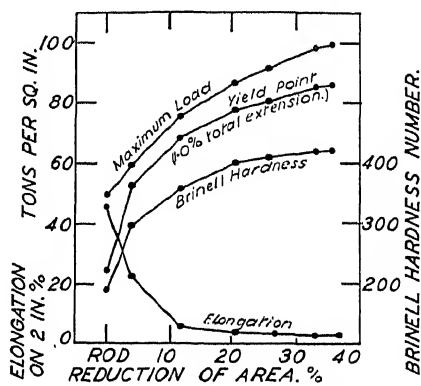


FIG. 270. Effect of cold-rolling on mechanical properties of austenitic Ni-Cr steel. (Rees.)

(*Journal of the Iron and Steel Institute.*)

between working and these properties is obtained. Fig. 269 determined by Pfeil (58) shows the effect of wire-drawing on the tensile strength of mild steel (0.11 per cent. C). Most curves of this kind are not extended to reductions of over 80 per cent. and when they are they do not usually show the rapid increase in strength indicated in this figure. Fig. 270 determined by Rees (285) shows the effect of cold-drawing on the tensile strength, yield-stress, hardness, and elongation of an austenitic nickel-chromium steel. Fig. 509 (Chapter XV) shows the effect of cold-drawing on the mechanical properties of copper and Fig. 532 in the same chapter shows its effect on brass. Fig. 271 determined by Kenyon and Burns (286) shows the effect of cold-rolling on the stress-strain curve of mild-steel sheet.

When steel is reheated after cold-working the first effect of the heating is to further increase the strength as shown in Fig. 75 and Table 18. Such heating between 200° and 300° C. is used in practice to increase the strength and elasticity (Fig. 76) of wire for springs and guns. This operation is known as 'blueing' because of the blue colour of the oxide formed in this range of temperature. At higher temperatures steel is softened, and although certain nickel alloys show an

increase in strength on heating after working, the general effect of heating non-ferrous metals is to eliminate the increased hardness and strength produced by working. The relations between the amount of working, the heating temperature, the time of heating, and the purity of the metal in so far as softening after working is concerned are discussed in Chapter IV, and illustrated in Figs. 510 and 511 and 533 to 540, Chapter XV. Softening does not take place gradually as the temperature is raised. Up to a certain temperature it occurs slowly and then becomes very rapid. This is accompanied by complete recrystal-

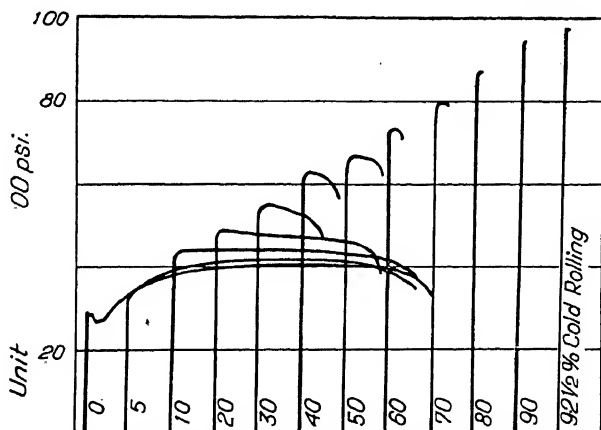


FIG. 271. Effect of cold-rolling on the stress-strain curve of mild steel.

(*Transactions of the American Society for Metals*,
Kenyon and Burns.)

lization, and the temperature at which it occurs decreases as the amount of deformation increases and to some extent as the time of heating increases. The temperature of rapid softening after a given amount of working varies with the composition of the metal and is raised rapidly by small amounts of impurities in pure metals. Thus Calvet (593) obtained the following results with two samples of pure aluminium: One sample containing 99.993 per cent. of aluminium began to recrystallize at about 200° C. and was completely recrystallized on heating for 10 minutes at 240° C. The other containing 99.9986 per cent. of aluminium recrystallized in 48 days at 25° C., in 6 hours at 60° C., and in 1 minute at 100° C.

In the cold-rolling or drawing of rods for machining the object is to obtain accurate dimensions and a good surface. Only a small reduction is performed in the cold, and it has the additional effect of improving the machinability of free-cutting steel and brass. In the drawing of wire the object may be to get the size and surface, and in many cases the drawn wire is finally annealed to restore it to the soft condition. Sometimes, however, the required final properties are obtained by a

hardening and tempering treatment as in the case of springs of silicon-manganese steel or twist drills made from high-speed steel wire. Frequently, the object of cold-working is to produce an increase in strength and stiffness as well as the necessary dimensions. This applies to high-strength steel wire used for springs, guns, pianos, and wire ropes, copper wire used for overhead conductors, and pressings of various kinds in aluminium, brass, cupro nickel, and mild steel. When a metal is cold-worked to a considerable extent it is said to be hard-drawn, -rolled, or -worked, and sheet material is marketed in various grades, i.e. quarter-hard, half-hard, three-quarters-hard, and hard according to the amount of work performed after the last annealing.

In the cold-working of alloys consisting of two constituents of different mechanical properties the factors discussed in connexion with hot-working are even more important. At cold-working temperatures brittle constituents are much more brittle than at hot-working temperatures, and if they are continuous or substantially so cold-working is impossible. If, however, the brittle constituent is discontinuous or has been previously broken up by hot-working then cold-working is possible. In connexion with this it should be noted that most of the deformation occurs in the ductile constituent, and as this has to flow round the brittle constituent the amount of strain-hardening produced by a given amount of working is increased. Thus, a given amount of cold-work hardens copper containing cuprous oxide more than pure copper. If the brittle particles are small and widely dispersed they undergo no during cold-working except in their distribution. Larger particles which present greater obstacles to the flow of the plastic constituent may, however, be broken up. Thus the hard particles of eutectoid which occur between the alpha dendrites in a cast Admiralty gun-metal are broken up when the alloy is deformed and the constituent fragments moved with respect to each other.

Low-carbon steel consists of particles of pearlite, which is relatively hard, distributed in a matrix of soft ferrite. When this alloy is worked, most, but not all, of the deformation takes place in the ferrite, which seems to flow round the pearlite as shown in Fig. 53. The pearlite is itself an aggregate consisting of alternating plates of ferrite and the brittle constituent cementite, and its deformation is another interesting example of the effect of work on alloys containing constituents of very different properties. Steels containing between 0.8 and 0.9 per cent. of carbon consist almost entirely of pearlite. When they are slowly cooled the plates of ferrite and cementite are relatively thick, and the metal does not deform easily. In a tensile test the strength is high, but the elongation and reduction of area are low. The metal cannot be cold-drawn. By increasing the rate of cooling the thickness of the ferrite and cementite plates may be greatly reduced. After this treatment the strength, elongation, and reduction in area are all increased, and the metal becomes very suitable for cold-drawing. Large quantities of

high-strength wire are made from such steel, and it is clear that its capacity for deformation depends on the presence of thin cementite plates. If these are thick they cannot be deformed without rupture, and in such a case the resulting fracture is large enough to provide a starting-point for a crack. If, however, the cementite plates are thin, and are supported on both sides by plates of ferrite, they bend quite readily and when they break the fractures are small and frequent. The purpose of the 'patenting' treatment is to produce thin cementite plates.

If breaking up a more or less continuous network of a hard constituent results in an increased capacity for deformation, it follows that alloys in which the plastic constituent is not hardened by working should be softened rather than hardened by this treatment. An example of this is furnished by certain alloys of lead. In order to increase the strength of this metal, and particularly its resistance to repeated stresses, small quantities of tin, cadmium, and antimony are added in various combinations. The binary systems formed by lead and each of these metals are eutectic systems with limited solubility of the added metal in the lead. The structure of the cast alloys, therefore, consists of dendrites of lead, containing certain amounts of the added metals in solid solution, outlined by thin films of eutectic. The alloys of tin and cadmium with lead are soft. Antimony is a hard metal, however, and alloys containing it are considerably harder than lead because of the distribution of the hard eutectic. Waterhouse and Willows (288) investigated the effect of cold-rolling on a series of lead alloys. The results were to some extent affected by a rise in temperature during rolling which tended to accelerate the self-annealing of the lead, but they established quite definitely that the cold-working caused a temporary hardening of the soft alloys and a permanent softening of the hard alloys. This is what would be expected. During rolling the hard eutectic outlining the lead dendrites would be broken up and the capacity for deformation improved. In alloys of less plastic metals this increased capacity for deformation would be more than balanced by the work-hardening effect. In lead, however, the amount of work-hardening is slight, so that the final result was a decrease in hardness resulting from the breaking up of the hard network.

The extent to which metals may be cold-worked, and the magnitude of the change in properties produced by a given amount of working, vary considerably with the composition, constitution, and structure of the alloy. The rate of the changes that take place after working is also affected to a pronounced extent by these factors. In general, the pure metals can be cold-worked to a greater extent and with a smaller increase in hardness than any of the alloys of which they are the basis. Primary solid solutions harden more rapidly than the pure basis metals, but as a rule they are capable of extensive deformation in the cold, as is illustrated by α -brass, α -bronze, α -copper-aluminium, and nickel-

copper alloys. Intermediate constituents of the β -brass type are rather more difficult to work than solid solutions and the other types of intermediate constituents are brittle. In complex aggregates containing two constituents of different properties the effects of working depend on their relative amounts and on their distribution.

Elements that enter into solid solution raise the recrystallization temperature and constituents that are not in solid solution have also a pronounced effect on recrystallization. In aggregates which contain a dispersed constituent it is only the continuous constituent that recrystallizes. The dispersed constituent simply undergoes globularization and particle growth. When steel is cold-worked the cementite plates in the pearlite are broken up. On reheating after cold-working the ferrite recrystallizes in the range of temperature between 520° and 560° C., but nothing happens to the cementite until the metal is heated above 600° C. Then the small fragments into which the plates have been broken by deformation begin to globularize under the action of surface tension, and as cementite is slightly soluble in ferrite, solution and re-deposition take place leading to the growth of certain of the particles at the expense of others. As the extent to which the plastic constituent is deformed by a given amount of work is increased by the presence of less plastic constituents, dispersed constituents tend to lower the temperature at which recrystallization begins. At the same time, however, they obstruct the growth of the new generation of crystals. It has been shown by Carpenter and Elam (289) that when commercially pure aluminium is annealed after severe cold-working, the impurities present at the boundaries of the original crystals retain the distribution conferred on them by the cold-working, i.e. they remain as thin longitudinal streaks. Because of this the growth of the new generation of crystals in directions perpendicular to them is obstructed. The new crystals tend therefore to be elongated in the original direction of working and only develop the normal equiaxed form after prolonged annealing. This obstructing effect of insoluble impurities is made use of in preventing grain growth in tungsten filaments. These are drawn in a range of temperature in which the effects are those of cold-working. In use they are maintained above the recrystallization temperature. If they are made from practically pure tungsten, grain growth proceeds during service and the filament tends to sag. To prevent this, various oxides which are insoluble in tungsten and non-volatile at the temperatures reached in manufacture or in use are added. Of these the one most frequently used is thoria. After the filament has been drawn the minute particles of thoria are arranged in rows in the direction of drawing. While the filament is in service, grain growth, particularly in directions perpendicular to that of drawing, is to a large extent prevented.

Attention has so far been confined to the effect of cold-working and annealing on structure and mechanical properties. The effect on

certain other properties may be described briefly. When a cast metal is consolidated by hot-working, the specific gravity is increased through the closing of gas and contraction cavities. When sound metal is deformed in the cold, however, a frequent result is a decrease in specific gravity, i.e. an increase in specific volume. There are cases, however, in which an increase in specific gravity due to working has been reported. It has further been shown by Alkins (290), and Alkins and Cartwright (291), that in copper and low-tin bronze a rise in specific volume in the earlier stages of working is followed next by a decrease, and finally by a rapid increase when the metal is cold-drawn to the limit of its capacity. The final rapid rise is probably due to the formation of cavities in the 'overdrawn' metal, but the preceding decrease is difficult to explain. Many such anomalies in the behaviour of metals still await an explanation, however, and it must suffice for the present to state that the usual result of working is a slight fall in specific gravity, generally of the order of 0.05–0.2 per cent.

The electrical resistance is slightly increased by cold-working, i.e. the conductivity is decreased. Electrolytic copper when hard-drawn has a conductivity about 2.5 per cent. less than that of the annealed metal, and an effect of similar magnitude is obtained with the other conducting metals silver and aluminium. Magnetic permeability is frequently affected to a pronounced extent by working. Even a slight amount of deformation tends to produce a marked decrease in this property and a small increase in remanent magnetism and coercive force. For this reason any deformation of those metals that have to be used for purposes requiring high permeability has to be avoided, and even such deformation as may occur in handling dynamo sheets is liable to produce a marked effect. The nickel-iron alloys of high permeability, i.e. Permalloy, Mumetal, and Hypernik, are very susceptible to the effect of deformation and many difficulties in their application have arisen from this.

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